Prediction of Wastewater Characteristics from Alkaline Combustion Wastes

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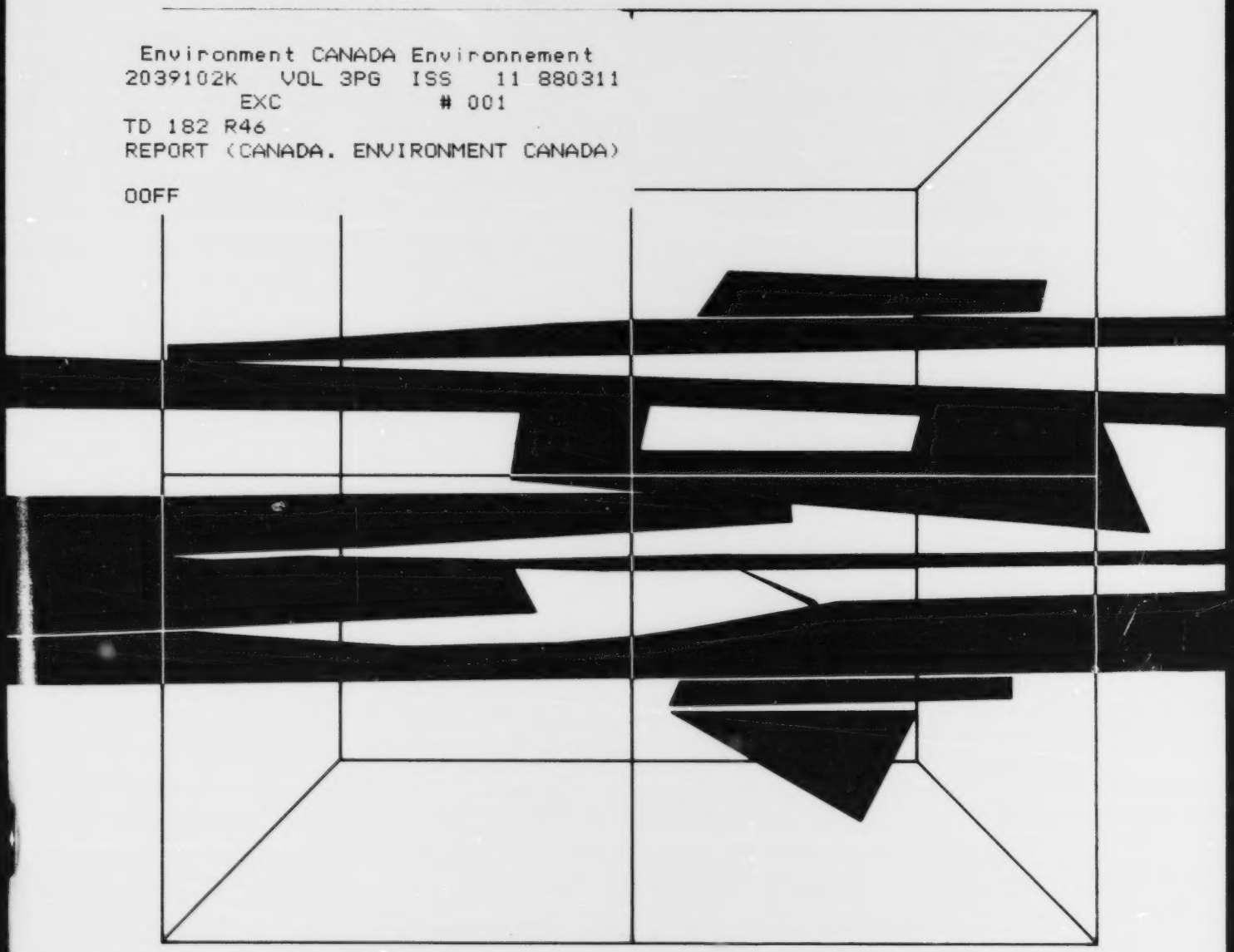

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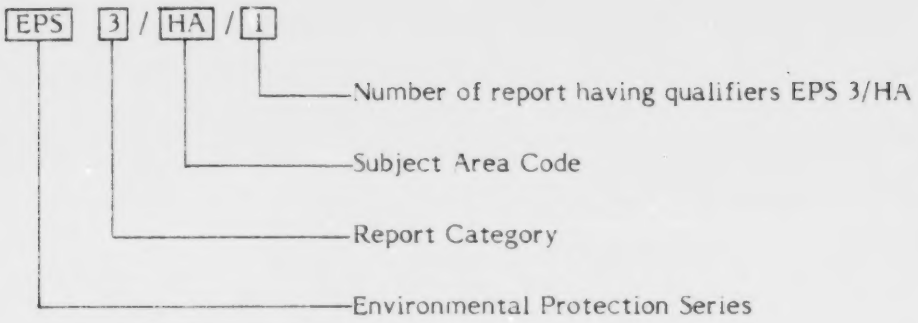

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PREDICTION OF WASTEWATER CHARACTERISTICS FROM ALKALINE COMBUSTION WASTES

by

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Mississauga, Ontario

for the

Industrial Programs Branch
Environmental Protection
Conservation and Protection
Environment Canada

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ABSTRACT

Atmospheric fluidized bed combustion (AFBC) is a rapidly developing technology which allows problem fuels to be combusted while achieving strict air emission requirements. The process will likely produce large volumes of waste which are as yet not well understood and for which optimum waste handling and disposal methods have not been identified. For these reasons, residues resulting from the pilot-scale combustion of a variety of fuels, including high sulphur coals and petroleum coke in beds of eastern or western Canadian limestones, were subjected to a characterization program.

The program included tests to characterize the physical, chemical, leachate and leachate toxicity properties of the AFBC residues. In addition, simple methods to predict the characteristics of combustion residue-contacted wastewaters were investigated. The effect of contact with the atmosphere on leachate chemistry and toxicity was also studied.

The results of the characterization studies were assessed in order to identify variations in wastes and their leachates, the implications of chemical reactions and the environmental consequences of AFBC waste management and disposal.

RÉSUMÉ

La combustion en lit fluidisé, à la pression atmosphérique, est une technique en pleine croissance qui permet de se débarrasser de combustibles à problèmes sans polluer l'atmosphère. Elle devrait probablement produire de gros volumes de résidus aux propriétés encore peu connues et pour lesquels les méthodes optimales de manutention et d'élimination restent à trouver. C'est pourquoi les résidus de la combustion en pilote d'une variété de combustibles, y compris de coke de pétrole et de charbons très soufrés, en lits de calcaire de l'est et de l'ouest du Canada ont été soumis à un programme de caractérisation.

Ce programme comprenait des essais de détermination des propriétés physico-chimiques des résidus, de leurs lixiviats ainsi que de la toxicité de ces derniers. En outre, on a exploré des méthodes simples qui permettraient de prévoir les caractéristiques des eaux usées mises en contact avec les résidus de la combustion. On a aussi étudié l'effet, sur les propriétés chimiques et la toxicité des lixiviats, de leur contact avec l'atmosphère.

Les résultats des caractérisations ont été évalusé afin de déterminer la variabilité des propriétés des résidus et de leurs lixiviats, les implications de leur réactivité chimique ainsi que les conséquences écologiques de la gestion et de l'élimination de ces résidus.

TABLE OF CONTENTS

		Page
ABSTRACT		iii
RÉSUMÉ		iv
LIST OF FIGURES		vii
LIST OF TABLES		viii
ACKNOWLEDGEMENTS		ix
1	INTRODUCTION	1
1.1	Project Objectives	2
1.2	Description of Samples	3
2	EXPERIMENTAL PROGRAM	4
2.1	Introduction	4
2.2	Physical Characteristics	5
2.2.1	Specific Gravity	5
2.2.2	Minimum Density	5
2.2.3	Particle Size Distribution	6
2.2.4	Moisture Content	6
2.3	Chemical Characteristics	6
2.3.1	Trace Chemical Characterization	6
2.3.2	Crystalline Composition	7
2.3.3	Exothermic Characterization	7
2.4	Leachate Characterization	7
2.4.1	Method of Leachate Testing	7
2.4.2	Aeration Experiments	8
2.4.3	Computerized Predictive Techniques	9
2.5	Aquatic Toxicity and Genotoxicity Characterization	13
2.5.1	Microtox™ Toxicity Assay	14
2.5.2	Algal Toxicity Assay	15
2.5.3	SOS Chromotest™ Genotoxicity Assay	16
2.5.4	*Daphnia magna* Toxicity Assay	18
3	RESULTS	20
3.1	Physical Characteristics	20
3.1.1	Specific Gravity	20
3.1.2	Minimum Density	20
3.1.3	Particle Size	21
3.1.4	Moisture Content	21
3.2	Chemical Characteristics	21
3.2.1	Trace Chemical Composition	23

		Page
3.2.2	Crystalline Composition	23
3.2.3	Exothermic Characterization	25
3.3	Leachate Characteristics	26
3.3.1	Leachate Composition	26
3.3.2	Aeration Experiments	27
3.3.3	Effect of Mixing Regime on Reaction	29
3.3.4	Results of Computerized Predictions	31
3.4	Leachate Aquatic Toxicity and Genotoxicity Characterization	33
3.4.1	Microtox™ Toxicity Assay	37
3.4.2	Algal Toxicity Assays	37
3.4.3	SOS Chromotest™ Genotoxicity Assay	37
3.4.4	*Daphnia magna* Toxicity Assay	37
4	DISCUSSION	38
4.1	Physical Characteristics	38
4.2	Chemical Characterization	39
4.2.1	Crystalline Characterization	39
4.2.2	Leachate Characterization	42
4.2.3	Aeration Experiments	44
4.2.4	PHREEQE Predictions	47
4.3	Leachate Toxicity and Genotoxicity Characterization	48
5	CONCLUSIONS AND RECOMMENDATIONS	51
5.1	Conclusions	51
5.2	Recommendations	52
REFERENCES		53
APPENDIX A	LABORATORY TEST RESULTS	55
APPENDIX B	RESULTS FROM COMPUTER MODELLING	75
APPENDIX C	Section 1 - Duplicate Analyses of Aquatic Toxicity and Genotoxicity Tests	99
	Section 2 - Multi-detector Laser Light Scattering Analysis	102

LIST OF FIGURES

Figure		Page
1	LABORATORY-SCALE AERATION EQUIPMENT	8
2	AFBC RESIDUE PARTICLE SIZE DISTRIBUTIONS	22
3	TYPICAL NEUTRALIZATION CURVE	28
4	EFFECT OF MIXING ON NEUTRALIZATION CURVE	30
5	RELATIONSHIP BETWEEN CaO CONTENT AND HEAT RELEASE	41
6	PRINCIPAL LEACHATE COMPONENTS	43
7	EFFECT OF MIXING ON REQUIRED AIR	46

LIST OF TABLES

Table		Page
1	DESCRIPTION OF SAMPLES	3
2	CHEMICAL COMPOSITION OF AFBC RESIDUES	24
3	CRYSTALLINE COMPOSITION OF AFBC RESIDUE TYPES	24
4	LEACHATE CHEMICAL COMPOSITION FOR AFBC RESIDUES	27
5	COMPARISON OF UNTREATED AND TREATED AFBC LEACHATES	29
6	SUMMARY OF RESULTS - PHREEQE LEACH TEST SIMULATIONS FOR CLOSED SYSTEM (no CO_2 contact) AND OPEN SYSTEM (atmospheric PCO_2) TRIALS	32
7	PROPORTION OF TOTAL SOLUBLE COMPONENTS DISSOLVED AT 20:1 (Liquid: Solids)	34
8	RESULTS OF AQUATIC TOXICITY AND GENOTOXICITY TESTS ON LEACHATES FROM AFBC WASTES	35
9	RESULTS OF MICROTOX™ TESTS ON UNTREATED LEACHATES FROM AFBC WASTES	36
10	COMPARISON OF LABORATORY-PRODUCED AND COMPUTER-SIMULATED LEACHATES	47
11	PRINCIPAL LEACHATE CONSTITUENTS AND LEACHATE TOXICITY OF UNTREATED AND TREATED LEACHATES	49

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1 INTRODUCTION

Atmospheric fluidized bed combustion (AFBC) technology is rapidly gaining acceptance for the combustion of problem solid fuels such as high sulphur coal. In this coal combustion process, coarsely crushed coal, together with limestone, is suspended in the combustion chamber through the injection of fluidizing air from below the bed. During combustion, the limestone is calcined to calcium oxide (CaO), which combines with both the sulphur dioxide (SO_2) released during combustion and oxygen to form calcium sulphate ($CaSO_4$). The control of sulphur emission is accomplished within the combustion chamber, which eliminates the need for add-on flue gas scrubber technology.

One limitation of the sulphur capture process appears to be the large quantities of solid residues produced. These are primarily composed of $CaSO_4$ and CaO and are quite different from ashes associated with pulverized coal combustion. Preliminary data (1,2) suggest that unconditioned bubbling bed AFBC solid wastes are relatively soluble and would produce well-buffered very high pH wastewaters, unlike those from pulverized high sulphur coal combustion wastes. Another unique property is the exothermic reaction when water contacts the AFBC wastes. The high heat releases are believed to be caused by the slaking or hydration reaction of the CaO portion of the wastes. Other unique properties such as swelling of the wastes when wetted, strength development in the residues and presence of calcium sulphide (CaS) have also been demonstrated.

The experience with bubbling atmospheric fluid bed combustion, therefore, is similar to that of flue gas desulphurization in that the most serious environmental concerns are likely to be associated with the handling, management and disposal of the resulting solid wastes. The unique properties of these wastes necessitates characterization studies in order to quantify their unusual properties and determine their behaviour in the environment.

A variety of fuels including high sulphur coals and petroleum coke have been combusted in beds of eastern and western Canadian limestones in pilot-scale AFBC units. The analyses of the resulting residues provides an opportunity to determine the impact of fuel and sorbent types on waste characteristics and to predict their behaviour when disposed of in the environment.

Limited experience with full-scale AFBC facilities in Canada has resulted in little opportunity to directly assess the effects of disposal techniques on the environment. At this time, the long-term behaviour of the fluidized bed combustion wastes must be

predicted based on characterization studies of pilot-scale produced residues. Predictive tools would potentially be very useful in quickly and cheaply assessing the likely behaviour of residues, particularly as part of a routine disposal practice.

Unfortunately, only few laboratory-scale predictive tests now exist. These are limited in their usefullness by their inability to predict waste behaviour in the environment. They require skilled laboratory personnel and analytical facilities and are costly and time consuming. Also, the procedures may represent only a limited number of disposal situations. One avenue available to overcome some of the limitations of laboratory-scale leaching testing involves the use of computerized chemical equilibria modelling. These models have the capability of rapidly predicting the leachability of wastes under varying disposal situations using only limited data as a starting point.

Before AFBC technology can proceed fully, the properties of the residues must be understood and potential difficulties with their disposal must be identified. From an operations perspective, the ability to predict waste behaviour after landfilling would be beneficial.

1.1 Project Objectives

The overall objective of this study was to characterize AFBC residues in terms of their physical and chemical properties, and to assess the impact of these properties on the chemical nature and biological toxicity of waste-contacted leachates.

The work plan was developed to fulfill the following specific objectives:

- to conduct a detailed study of the physical, chemical, exothermic and leaching characteristics of AFBC solid waste samples using laboratory-scale equipment;
- to determine the effect of atmospheric contact on the leachate characteristics and assess the potential for use of this effect to treat and reduce the toxicity of the leachates;
- to assess simplified methods to predict the characteristics of combustion residue-contacted wastewaters before and after contact with the atmosphere; and
- to assess the results of the characterization studies to identify variations in wastes and leachates, implications of chemical reactions, and the environmental consequences of waste management and disposal.

Based on their chemical characteristics, including: pH, TDS, alkalinity, calcium and sulphate concentrations, leachates from nine of the residues were selected for further experiment. These tests were designed to assess:

a) the effects of aeration on leachate chemistry;

b) the utility of computerized chemical equilibria models to assess leachability; and

c) the potential for the reduction in aquatic toxicity and genotoxicity of the leachates by the use of aeration as measured by rapid screening tests.

One of the nine leachate samples was selected for additional study to identify the effects of mixing on the aeration reaction.

1.2 Description of Samples

The AFBC residue samples characterized during this study were generated at the Queen's University pilot scale combustor between November 1984 and October 1985. The combustor is described in detail by Becker et al. (3). A variety of fuels including high sulphur eastern Canadian coal and petroleum coke were combusted in beds of eastern or western Canadian limestones. In all but one case, spent bed, cyclone and baghouse capture residues were analyzed from each test run. The exception was due to limited sample availability.

The fuel and sorbent used for each combustor run and the types of samples which were collected for the characterization program are summarized in Table 1.

Leachate samples from Test Runs 1, 5 and 8 were used in the additional study of aeration reactions and computer modelling. Leachate from Test Run 1 baghouse material was used to evaluate the effect of mixing on the aeration reaction.

TABLE 1 DESCRIPTION OF SAMPLES

Test Run	Date of Combustion Test (d/m/yr)	Fuel	Sorbent	Sample Types Characterized
1	11/09/84	Syncrude	Athabaska	Bed Cyclone Baghouse
2	04/03/85	Devco	Sysco	Bed Cyclone Baghouse
3	composite* 12/11/84 15/11/84 19/11/84	Kentucky No. 9	Reed	Bed Cyclone Baghouse
4	18/12/84	Devco	Calpo	Bed Cyclone Baghouse
5	24/07/85	Devco	Havelock	Bed Cyclone Baghouse
6	03/06/85	Minto	Havelock	Bed Cyclone Baghouse
7	22/05/85	Evans	Havelock	Bed Cyclone **
8	24/10/85	Lingan	Sysco	Bed Cyclone Baghouse

* Due to limited sample, a composite of three combustion runs was used in the characterization program.

** Insufficient baghouse sample for characterization.

2 EXPERIMENTAL PROGRAM

2.1 Introduction

The experimental program for this study consists of three main components: 1) characterization of the AFBC residues; 2) the application of computerized predictive techniques; and 3) implications of leachate/air interactions. The combustion residues were initially characterized to provide data on their physical, chemical and leaching properties. In a practical sense, knowledge of the physical properties would be useful in assessing the behaviour of the residues in a geotechnical or waste disposal situation since these properties would govern the rate and volume of leachate which would be produced. The particle size data would permit inference to be made on the permeability and compactability of unconditioned residue. The density of the waste would permit estimates to be made of the disposal area volume. Optimum waste disposal would take advantage of the wastes' geotechnical properties and would minimize the amount of leachate which would need to be collected and possibly treated.

In terms of the chemical characterization, knowledge of the trace chemical composition allows an assessment to be made of the potential to generate contaminated wastewaters. The crystalline composition of the residues would likely control the major chemical properties of waste-contacted waters such as pH, total dissolved solids (TDS) and principle dissolved species. The potential heat release hazard can be quantified using the exothermic testing.

The leaching protocol used can assist in predicting the chemical characteristics of waste-contacted waters. This test procedure simulated a situation where there is a large waste surface area in contact with water and leachate contaminant concentrations are allowed to reach equilibrium with the solid waste. This would be considered a worst case situation.

The biological toxicity of leachates produced using this protocol was evaluated to assess the potential effects of waste-contacted waters on the environment.

As previously mentioned, since all residues were subjected to the same characterization program, residues resulting from the combustion of a number of fuel/sorbent combinations can be compared and contrasted in terms of their chemical composition and leachability.

The second component of the experimental program was the use and evaluation of a computerized predictive leaching model. This approach has the capability

of fast tracking the assessment of residue leaching without conducting laboratory testing and is based on the chemical composition of the wastes, since they control the nature of leachates that would be produced. Such a technique would permit leaching under varying conditions to be rapidly evaluated in a cost efficient manner.

The third component of the program was the evaluation of leachate/air interactions. It is known from previous studies that contact of FBC leachates with air can lead to significant changes in leachate characteristics. The chemical characteristics and biological toxicity of leachates, therefore, were evaluated under conditions where air had been excluded and where contact with air had been promoted by aeration. This permitted identification of the range of leachate characteristics which could result from contact with the atmosphere. Aeration was also evaluated as a potential leachate treatment process.

2.2 Physical Characteristics

Laboratory testing was conducted to characterize the physical properties of the AFBC residues. The procedures used to determine the specific gravity, minimum density, particle size distribution and water content are described in the following.

2.2.1 Specific Gravity. The specific gravity of a solid may be defined as a ratio of the weight in air of a given volume of solids at a stated temperature, to the weight in air of an equal volume of distilled water at a stated temperature. Specific gravity determinations were carried out on each of the 23 samples after oven drying.

Kerosene was used in the testing instead of distilled water, in accordance with Note 3 of ASTM D854-83, (4) with an appropriate correction applied to account for the difference in relative density between distilled water and kerosene. The results of the testing can be interpreted as the specific gravity of a single residue particle.

One sample, S-B-5, was tested in an "as received" condition. This was done to determine whether the specific gravities of the residues changed as a result of the drying at 105°C prior to testing.

2.2.2 Minimum Density. The objective of the minimum density test is to determine the density of a material in the loosest state of compactness using a standard laboratory procedure that prevents bulking and minimizes particle segregation.

The procedure used was ASTM D4254-83, (Method A) (4). This method was originally designed to control the placement of sand-sized particulate material and

provides information on the materials' densification properties. Samples were tested in the "as received" condition.

2.2.3 Particle Size Distribution. The particle size distributions were determined following ASTM D422-63 (4). This involves the use of both mechanical sieve screening and hydrometer testing. Sieve screens were used to size particles greater than 200 µm. For smaller-sized particles a hydrometer was used. The hydrometer analyses were carried out using a 50-g sample passing No. 20 (850 µm) sieve, pretreated with sodium hexametaphosphate for 24 hours, and mechanically stirred for eight minutes using distilled water.

The results for the bed and cyclone residues showed an increase of "percent finer than" from the 75 µm to the 45 µm sizes. This increase is inconsistent with normal particle size distribution. Therefore, a second set of tests was carried out on these series of samples using 100 g of material using distilled water but without sodium hexametaphosphate, and sieved down to the 270 (53 µm) sieve. These results showed a similar increase of "percent finer than" from the mechanically-sieved fraction (e.g., down to the No. 270 sieve), for the first four minutes of the hydrometer test. The significance of this will be discussed in Section 4.1.

2.2.4 Moisture Content. In order to perform the specific gravity and particle size analyses, it was necessary to dry the ash samples. The water content determinations were made for the samples using the weights of the samples before and after oven drying.

The water content of a soil is defined as the ratio, expressed as a percentage, of the weight of water in a given soil mass to the weight of solid particles. ASTM D2216-80 (4) was the procedure used for this testing.

2.3 Chemical Characteristics

In order to chemically characterize the residues, their trace chemical, crystalline and exothermic characteristics were determined. The methods used are described in the following.

2.3.1 Trace Chemical Characterization. The trace chemical composition of the residues was determined primarily using inductively coupled argon plasma spectroscopy (ICAP) and flame atomic absorption (AA). Both procedures are preceded by an appropriate digestion. ICAP has the advantage that a large number of elements can be simultaneously determined in one step. AA was used to improve the detection limits for several parameters for which ICAP is less sensitive.

A quality control program for these analyses consisted of the use of a standard reference PCF fly ash (NBS material no. 1633a). There is no NBS AFBC standard

material. This standard material was analyzed using the same methods as the other residues with the results compared to the NBS published data.

2.3.2 Crystalline Composition. The principal crystalline composition of the residues was determined primarily using X-Ray diffraction (XRD) analyses. These analyses were supplemented by neutron activation, X-Ray fluorescence and wet chemistry methods to confirm the XRD results.

The X-Ray diffraction technique only reveals the compounds present in crystalline form (5). Noncrystalline or amorphorous forms are not quantified.

2.3.3 Exothermic Characterization. Each residue was subjected to a calorimeter test to determine its exothermicity, also known as the heat of reaction or loss of enthalpy per unit mass. The procedure used was similar to that described in ASTM C110-76a(4) except that the amounts of water and residue used were different. In this method, to a known mass of water contained in the Dewar flask (calorimeter) a known mass of residue was added to provide a liquid to solid ratio of 5:1. The temperature of the well-stirred mixture was followed as a function of time for at least 30 minutes or until less than 0.5°C temperature change was observed among three consecutive readings. Deionized water was used as the liquid.

2.4 Leachate Characterization

2.4.1 Method of Leachate Testing. Each residue was subjected to the leaching protocol developed at the Wastewater Technology Centre by Coté and Constable (6). This procedure involves leaching the wastes in a 20:1 liquid-to-solid ratio for 24 hours using deionized water. The waste/leaching medium mixtures are radially rotated in closed bottles with about a 10% headspace. This minimizes the exchange with atmospheric gases but maximizes waste mixing. This protocol is not capable of assessing the effects of residue strength development on the rate of leachate production or characteristics.

Following settling, the supernatants were sampled and filtered through 0.45 mm paper and the leachates were chemically analyzed. The procedures used included ICAP, flame atomic absorption, ion chromatography, wet chemistry and instrumental methods.

The quality control program for the leachate chemical characterization consisted of the analyses of split samples and the reanalysis of selected samples. Through this procedure, the precision of the analytical results was controlled.

2.4.2 Aeration Experiments. The laboratory-scale apparatus used to conduct the aeration experiments is shown in Figure 1. A porous stone diffuser was connected to a compressed air supply and immersed in 1 L of sample in a 1.5-L battery jar. The pH was monitored and recorded continously on a strip-chart recorder. The air was supplied at a rate of 0.113 m^3/h. The sample was mechanically agitated using a two-bladed rectangular impeller producting a radial mixing pattern. Experiments were conducted at room temperature (20°C). Following about a twenty hour reaction time, the aerated leachates were settled with the supernantant and solids sampled for subsequent analysis.

In order to investigate the effects of mixing intensity on the aeration reactions, the same overall procedure was used. The rate of mechanical agitation was adjusted to vary the mixing over a range of "G" values from 100 to 2000 s^{-1}. The value "G" defines a velocity gradient and is used as a measure of the intensity of turbulence during mixing.

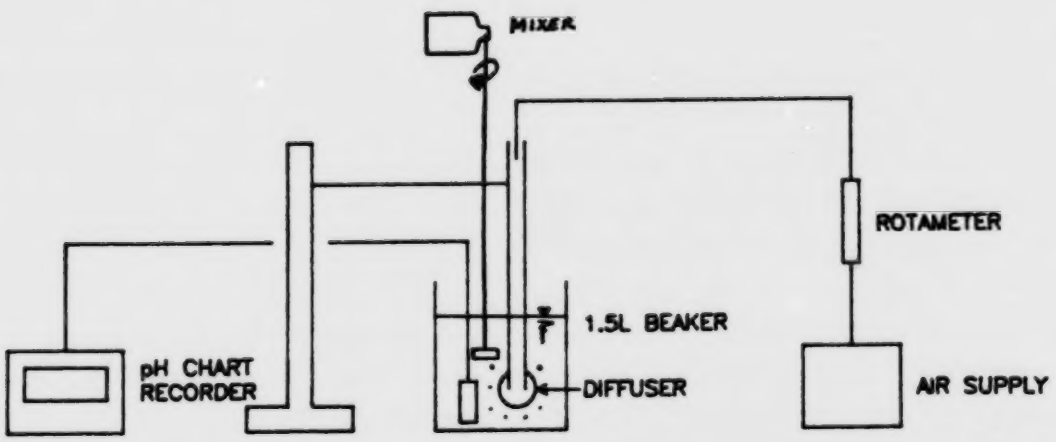

FIGURE 1 LABORATORY-SCALE AERATION EQUIPMENT

2.4.3 Computerized Predictive Techniques

One task of this study was to investigate techniques to predict the characteristics of leachates resulting from the contact of water with AFBC residues with and without contact with atmospheric gases. Some form of computerized chemical leaching model was thought to be the most expedient means to predict the leachability of the AFBC residues.

A procedure was developed whereby the leachate chemical characteristics resulting from a 20:1 liquid-to-solid ratio leach test of AFBC residues could be simulated using a minimum of solid phase chemical characterization data. The X-Ray characterization data served as the input to a computer model called "PHREEQE", developed by the U.S. Geological Survey (7), and designed for calculation of interactions between water and mineral (solid) phases. The procedure was used to simulate both open and closed system conditions, with respect to atmospheric carbon dioxide (CO_2.) In the closed system case, no CO_2 was allowed to enter or leave the theoretical reaction vessel during the test. In the open system case, atmospheric CO_2 was allowed to interact completely with the leaching test, attaining chemical euilibrium between the leaching solution and the atmospheric partial pressure of CO_2 (PCO_2), $10^{-3.5}$ atmospheres.

The main component of the simulation procedure was the geochemical modeling program "PHREEQE", which stands for pH-redox-equilibrium-equations. PHREEQE can be used to calculate pH, redox potential, and mineral saturation status in aqueous solutions, as well as mass transfer between solid phases (minerals) and the solution phase during a reaction. In addition, the chemical compositon of solutions in equilibrium with both solid and/or gaseous phases can be calculated.

Experimental Approach. The procedure developed to simulate 20:1 (liquid to solid) leaching of AFBC residues had three components:

(1) Express the weight percent of each chemical compound determined by the X-Ray analysis in terms of moles of soluble mineral available per litre of distilled water. These calculations are presented in Appendix A.

(2) Convert the moles of the compound per litre of water into a formulation compatible with the geochemical model PHREEQE.

(3) Conduct the numerical simulations using the PHREEQE program, for the specified conditions (i.e., open or closed with respect to CO_2), and maintaining concentrations of dissolved ions such that the solution is not supersaturated with respect to any of the relevant mineral phases.

The procedure was developed to simulate the following experimental conditions:

(1) 20:1 liquid-to-solid ratio;

(2) temperature of 20°C;

(3) deionized water leaching media, pH of 6.2; and

(4) without contact of atmospheric CO_2, and at equilibrium with atmospheric CO_2.

In order to facilitate the numerical simulation pe (-log of electron activity) was fixed at a value of 7.0, representing moderately oxidizing conditions in terms of natural aqueous systems.

The characterization of ash solids produced analytical results for the following substances: 1) calcium sulphate, $CaSO_4$; 2) calcium sulphide, CaS; 3) calcium carbonate, $CaCO_3$; 4) calcium phosphate, $Ca_3(PO_4)_2$; 5) calcium oxide, CaO; 6) iron oxide, Fe_2O_3; 7) other, described as mainly silica, SiO_2 and silicates; and 8) loss-on-ignition, described as primarily unburned carbon. The numerical treatment of each of these components is discussed individually in the following:

(1) $CaSO_4$ is treated as soluble Ca^{2+} and SO_4^{2-} available to dissolve directly in the leaching medium.

(2) CaS is treated as Ca^{2+} and S^{2-} (-II oxidation state), which is available to undergo oxidation via the reaction:

$$CaS + 2O_2 \longrightarrow CaSO_4$$

in aqueous solution. Unlike the oxidation of pyrite, which produces acid, the oxidation of CaS is essentially nonacid-forming, except for a small amount of H^+ produced from the hydrolysis of Ca^{2+} by water. In this respect, the oxidation of CaS is analogous to the oxidation of galena (PbS) and sphalerite (AnS), which, in natural occurrences of weathered mineralized deposits, are found to be only slightly acidic.

(3) $CaCO_3$ is treated as the mineral calcite, which undergoes dissolution and precipitation reaction as Ca^{2+} and CO_3^{2-}. These reactions are strongly dependent on pH and the equilibria of carbonic acid, H_2CO_3.

(4) $Ca_3(PO_4)_2$ is found in nature, although its occurrence is rare. The solubility of calcium phosphate is generally controlled by the mineral apatite, which has the chemical formula $Ca_5(PO_4)_3OH$, and is properly named hydroxyapatite, since either F^- or Cl^- can substitute for OH. The dissolution and precipitation reactions of $Ca_3(PO_4)_2$ are analogous to those of $CaCO_3$, except in this case phosphate

dissolution/precipitation is influenced by the dissociation equilibria of phosphoric acid (H_3PO_4). This acid has three dissociation steps, with undissociated H_3PO_4 dominant only at very low pH (less than about 2.1). $H_2PO_4^{2-}$ is the dominant phosphate anion in the pH range between 2.1 and 7.2, and between pH 7.2 and about pH 12.4 HOP_4^{2-} is the dominant form of phosphate. For the purposes of numerical simulation using PHREEQE, 1 mole of $Ca_3(PO_4)_2$ is represented as 3 moles of Ca^{2+} and 2 moles of PO_4^{3-}.

(5) CaO readily reacts with water to form $Ca(OH)_2$, via the reaction:

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

Consequently, the presence of large amounts of CaO generally correspond to high pH conditions. Because of the nearly instantaneous conversion of CaO to $Ca(OH)_2$ in the presence of water, $Ca(OH)_2$, as soluble Ca^{2+} and OH^- are considered as the input components for the simulations. The numerical technique used by the program PHREEQE, however, does not consider the mass balance of oxygen or hydrogen, and consequently does not allow OH^- to be input directly to the model as a reaction constituent. It is possible, however, to input OH^- indirectly to the model by utilizing a charge-neutralizing feature of the program: if a reaction input to the model is not electrically neutral (i.e., does not have an equal number of moles of -ve and +ve charge), then the program is designed to add hydrogen ion (H^+) to neutralize an excess of negative charge. Conversely, the program adds hydroxide (OH^-) to offset an excess of positive charge. Consequently, to input $Ca(OH)_2$ to the simulation reaction it is only necessary to enter Ca^{2+}. The program automatically adds sufficient OH^- to produce an electrically neutral (and chemically correct) reaction.

(6) The precise form in which the Fe_2O_3 is present is not known, as reported in the X-Ray analyses. Consequently, it was assumed that all Fe_2O_3 was in the form of hematite, a common mineral found in both sedimentary and other rocks, and an accessory mineral that might logically be associated with coal beds. For reasons discussed previously, the oxygen component of Fe_2O_3 cannot be input directly to the numerical reaction. Consequently, the reaction is entered as only Fe^{3+}. In this case, however, inert electrical charge is also added to produce an electrically-balanced reaction input. In order to compensate for the absence of oxygen in the reaction, the simulations specify saturated conditions with respect to hematite.

In this way, the program automatically provides enough oxygen to precipitate hematite and maintain conditions of saturation with respect to hematite.

In the case of one sample, run No. 5 baghouse residue, the Fe_2O_3 content was exceptionally high at 23.0%. Preliminary simulations for this sample showed a large degree of hydrolysis associated with the input of such a high Fe^{3+} content, and the resulting pH of 2.1 was considered to be unreasonable. To compensate for this effect, for this sample only, Fe_2O_3 was not input directly to the reaction, but rather saturation with respect to hematite was specified as a constraint on the solution. Since all of the samples at all of the reported Fe_2O_3 levels showed saturation with respect to hematite, this approach was considered to be quite reasonable and probably most representative of either laboratory or natural leaching conditions.

(7) The category identified as "other" constituents was indicated in the analytical report as representing "mainly SiO_2 and silicates". The uncertainty in the nature of these silicates called for some degree of interpretation to be made in determining how to account for these constituents in the numerical simulations. Preliminary simulations treated all of the "other" component as amorphorous SiO_2, and aqueous concentrations of SiO_2 or silica acid (H_4SiO_4) were limited by the solubility of amorphorous silica (silica gel). Results of these simulations showed very high silica concentrations, in excess of 10 000 mg/L, in most of the closed-system samples. This reflected the high degree of solubility of silica in the pH range of 12 to 13. It was concluded that such an extreme case utilizing the most soluble form of silicate mineral was, probably, not representative of the AFBC waste material.

To better represent the silicate portion of waste, it was assumed that this constituent was composed primarily of potassium-feldspar (microcline), a potassium aluminum silicate that is very commonly found in sedimentary rocks. Since there was no analytical data available to provide quantitative support for this assumption, the simulations were conducted so that the aqueous solutions were allowed to dissolve potassium-feldspar up to levels of saturation. That is, no analytical input of silicate was utilized in the numerical "reaction", rather saturation with respect to microcline was specified as one of the constraints on the solution. This approach gives rise to concentrations of dissolved K^+ and Al^{+3} that constitute approximately 5% of the dissolved solids in the closed-system simulations, but are not present in the open-system cases.

Unless analytical or experimental evidence can provide some justification for modifying the form of the silicate and/or the degree of saturation permitted, it is

assumed that this approach will provide a reasonable estimation of the contribution of "other silicate" constituents.

(8) The analysis called "loss-on-ignition" is said to represent mainly unburned carbon. This carbon, having remained unoxidized after passing through the AFBC combustor, is assumed to be highly refractory and nonreactive. Consequently, in terms of reactions in low temperature aqueous solution, any reactions of such carbon are likely to be insignificant; therefore, the presence of unburned carbon was ignored for the simulation of leaching tests.

The net input to the simulation was the overall reaction that is the sum of reactions described under points 1 to 7 previously described. The result of this summation is a single, net reaction with nine components:

(1) Ca^{2+}, from $CaSO_4$, CaS, $CaCO_3$, $Ca_3(PO_4)_2$ and $Ca(OH)_2$;
(2) SO_4^{2-} from $CaSO_4$;
(3) S^{2-} from the oxidation of CaS;
(4) O_2 from the oxidation of CaS;
(5) CO_3^{2-} from $CaCO_3$;
(6) PO_4^{3-} from $Ca_3(PO_4)_2$;
(7) Fe^{3+} and
(8) electrons (e^-) from Fe_2O_3; and
(9) SiO_2, from "other" silicates.

As an example of PHREEQUE input, Appendix B contains a listing of the contribution of each constituent to the net reaction, for the simulation based on sample S-B-1.

The simulation procedure actually consists of two steps. In the first step, the whole reaction determined from the analytical results is added to distilled water, free of any saturation constraints. In the second step, mineral saturation constraints and CO_2 conditions (where desired) are imposed, and supersaturated solid phases are allowed to precipitate. Separate two-step simulations were conducted for the closed system and open system (with respect to CO_2) cases.

2.5 Aquatic Toxicity and Genotoxicity Characterization

Leachates were subjected to a battery of three aquatic toxicity tests (two sublethal and one acute) and one genotoxicity test. A battery approach rather than a single-tier characterization was selected in order to extend the range of physiological functions and sensitivities which were to be monitored. The toxicity of both untreated

and treated (aerated) samples was determined to demonstrate toxicity reduction during treatment. In addition, two samples were neutralized with mineral acid so a comparison between aeration and acidification as treatment methods could be made. As a supplement to the test battery, the algal assays were also analyzed by multi-detector laser light scattering. This analysis is described in Appendix C.

2.5.1 Microtox™ Toxicity Assay. The Microtox™ assay is a sublethal toxicity bioassay using bacteria. Bulich (8) reported that results of Microtox™ tests have agreed well with fish toxicity tests and that in a study concerning biomaterials testing, the Microtox™ test appeared to be even more sensitive than the tissue culture cytotoxicity test.

This system uses freeze-dried cultures of a strain of *Photobacterium phosphoreum*, a luminescent bacterium. Under normal conditions, the organisms continuously produce light which can be measured with a photometer. The bioluminescence of this organism can be considered a branch of its electron transport system as it is coupled via reduced flavin mononucleotide $FMNH_2$. $FMNH_2$ is one of the cosubstrates of the enzyme luciferase which catalyzes the luminescent reaction in photobacteria. When low levels of a toxicant interfere with the organism's metabolism, its light output decreases. Since the light reduction is proportional to the amount of toxicant present, the relative toxicity of a sample can be calculated from photometer readings.

Analyses were conducted using Microtox™ reagents and cuvettes (Microbics Inc.). Analyses were conducted according to the manufacturer's protocol as follows:

Measurement of light from the Microtox™ reagent (a luminescent bacterial species) was performed using a Turner Designs Model 20 Photometer connected to a recirculating water bath (Lauda Model RM3, Brinkman Instruments) to maintain the Photometer reaction chamber at 15.0°C.

Prior to analysis, each sample was adjusted to contain 2.0% NaCl by addition of 22% NaCl solution. A dilution series of the sample was then prepared in 2% NaCl. The series was prepared in glass cuvettes and held in a cooling block maintained at 15.0°C.

Another series of cuvettes, each containing 500 µL of a suspension of Microtox™ bacteria was prepared from a stock suspension maintained at 4°C. After these cuvettes had been held in the cooling block for 15 minutes, the light emitted from each cuvette was measured. Next, 500 µL from each sample dilution were added to a cuvette containing the Microtox™ bacteria and mixed. This procedure was performed in

duplicate. The light emitted from the bacteria was measured after 5 and 15 minutes exposure to the sample.

The results of the assay were expressed as EC_{50} values. The EC_{50} is the effective concentration (as a percentage) of a sample which causes a 50% response (compared to a control) for the biological parameter being assessed. For this assay the EC_{50} values for the 5 and 15 minute exposure periods were calculated by computer to determine the percentage of sample which caused a 50% reduction of light relative to a control which received 500 µL of 2% NaCl instead of sample.

The computer program to determine this calculation was derived from a program in the Microtox™ manufacturer's literature. First, "gamma" ratios (i.e., light remaining ÷ light lost, were calculated for each sample concentration tested.

Following logarithmic transformation, the relationship between "gamma" and sample concentration is linear. EC_{50} values (gamma = 1.0), and 95% confidence intervals, therefore, can be determined by linear regression and least squares methods.

2.5.2 Algal Toxicity Assay. This test was included in the test battery to represent primary producers. *Selenastrum capricornutum* was selected as the test organism because it has many attractive features, including: good sensitivity to toxicants; a characteristic relatively constant morphology; a tendency to remain in suspension without agglomeration; and capable of growth in both oligiotrophic and eutrophic aquatic systems.

Algal growth inhibition was tested using a microplate method described by Blaise (9).

Stock cultures of *Selenastrum capricornutum* (ATCC No. 22662) for toxicity testing were grown in a synthetic nutrient medium and maintained in logarithmic growth phase.

Prior to analysis, serial-halving dilutions of sample ranging from 100% to 0.098% were prepared in sterilized, double-deionized water.

Eight 200 µL replicates of each dilution were distributed across a microtiter plate by means of a multi-channel pipettor. To serve as controls, 16 wells were also innoculated with 200 µL of sterilized, double-deionized dilution water.

Each well, except eight of the control wells, was innoculated with 20 µL of algal innoculum to produce a final cell concentration of 20 000 cells/mL. Algal innoculum had been prepared by centrifuging an algal stock culture and resuspending it to achieve the desired cell concentration in $NaHCO_3$ (15 mg/L). Before addition to the sample

aliquots, this suspension was diluted by an equal volume of a synthetic nutrient concentrate.

Following the innoculation, the plates were sealed in plastic bags and placed under "cool-white" fluorescent light to provide approximately 4300 lux. The plates were incubated for four days during which time the contents of the wells in each plate were mixed daily to ensure proper cell contact with the solutions.

At the end of the incubation period, the wells were visually inspected. A series of wells which appeared to include the range of 0 to 100% algal growth inhibition were selected for cell counting. Cell counts were determined for a minimum of three wells on each sample concentration. Each cell count was compared to the control plate and the percent inhibition was calculated using the equation:

$$\text{percent inhibition} = \frac{(\text{control cell count} - \text{sample cell count})}{\text{control cell count}} \times 100\%$$

The sample concentration versus percent inhibition was plotted on log probit paper. The EC_{50}, the sample concentration which caused a 50% inhibition of algal growth, was estimated from this plot.

For most types of samples, it is possible to perform the log-probit transformation of the data and calculate mathematically an EC_{50} with 95% confidence intervals by linear regression and least square analysis. However, this procedure requires at least two graph points to be between the total effect (100% inhibition) and no effect (0% inhibition) concentrations. The combustion waste leachates produced a very steep toxicity response curve, and in the algal assays, only one concentration fell between the total and no effect concentrations. Although moving average transformations can circumvent this difficulty in conventional whole animal testing, it could yield misleading results when applied to algal assays. The number of test organisms in algal assays is several orders of magnitude greater than in whole animal tests. Since the number of test organisms (rather than just a ratio of dead to living organisms) plays an extremely influential role in moving average calculations, it was a concern that an analysis based on this type of transformation might place a misleading bias on the confidence limit.

Consequently, instead of calculating 95% confidence limits for the algal EC_{50}, confidence limits consisting of concentrations which caused 0% and 100% inhibitions are reported in the results.

2.5.3 SOS Chromotest™ Genotoxicity Assay. Like the Ames test, the SOS Chromotest™ is a bacterial test. However, the SOS Chromotest™ uses genetically

engineered bacteria which have had a foreign gene inserted in the region of their DNA repair genes. This foreign gene codes for the enzyme beta-galactosidase. When the genetically engineered bacteria in the test are exposed to genotoxic agents, lesions are produced in their DNA. Like all organisms, the bacteria respond immediately by activating DNA repair mechanisms and, as a consequence, the enzyme from the foreign gene is also synthesized. The presence of this enzyme is detected via colourmetric reaction; therefore, the degree of genotoxicity in a sample becomes directly related to colour production.

A commercial kit for conducting this procedure has been produced by Orgenics Limited (Israel). The "blue" kit was used for testing the genotoxicity of the leachates and the protocol recommended by the manufacturer was followed.

The procedure is initiated by rehydrating two vials of freeze-dried test bacteria and incubating them at 37°C for 3.5 hours. One vial is rehydrated for use with S-9 liver homogenate activation mix, while the other is used for testing without S-9.

Meanwhile, serial halving dilutions of sample are prepared in 10% DMSO (dimethylsulphoxide) in sterile 0.85% saline. Ten µL of each dilution are added to the wells of a microplate. 4NQO (4-nitroquinoline) and 2AA (2-amino-anthracine) are tested as positive controls, while sample diluent is included as a negative control.

At the end of the preincubation period, 100 µL of test bacteria are added to the sample aliquots. This procedure is repeated to the bacterial suspension to which S-9 metabolic activation mix has been added. The microplate is incubated for two hours at 37°C.

Toxicity and genotoxicity (induction of SOS DNA repair genes) is measured by means of colourmetric assays for alkaline phosphotase and beta-galactosidase. Alkaline phosphotase is an enzyme which is constitutive to this *E. coli* strain and its measurement determines whether growth inhibition has occurred. Beta-galactosidase is the enzyme from the foreign gene inserted in the region of the DNA repair genes, and its production indicates that DNA repair has been initiated.

To determine the genotoxic threshold concentration caused by a sample, readings for eight negative controls are first measured. The threshold is the concentration of sample which produces a colour reaction two standard deviations greater than the average obtained for the negative controls.

2.5.4 *Daphnia magna* Toxicity Assay. The use of this organism in toxicity testing is not only due to its high and often unique sensitivity to toxicants, but also its important ecological position.

Daphnia magna is a pelagic freshwater crustacean commonly known as cladocerns. This group of crustaceans are among the dominant consumers of primary producers. Cladocerns are present in oligiotrophic and eutrophic lakes, in ponds and in reservoirs where they constitute a food source for both invertebrate and vertebrate predators. They are therefore central to many freshwater food webs.

The 48-hour acute lethality test for *Daphnia magna* was conducted in static mode using U.S. EPA guidelines (10). Suggested procedures for *Daphnia* testing by Buikema et al. (11) were incorporated.

Daphnia magna were obtained from monoculture stocks at the Canadian Centre for Inland Waters, Great Lakes Biolimnology Laboratory in Burlington, Ontario. Taxonomic verification was completed using an invertebrate key (12).

Daphnia stocks were fed a diet of a mixture of *Selenastrum* and *Chlorella* algae every 48 hours in glass culture aquaria containing laboratory dilution water held at 20 ± 1°C. The photoperiod was maintained at 12 hours light, 12 hours dark. Water for culture was dechlorinated Mississauga tap water which is chemically analyzed monthly for metals, selected organics and nonspecific parameters.

The *Daphnia* culture was actively reproducing and no ephippial (sexual) eggs had been generated since the culture was initiated (one year). Based on general observations from other test preparations, four to six young were being produced per adult.

Gravid (egg-bearing) adults selected from the stock culture were isolated in 50-mL vessels containing laboratory dilution water and first instar (brood) daphnids were collected 24 hours later for testing. Different adults provided first instars for definitive tests.

The definitive tests were completed using the 24-hour old *Daphnia* instars generated. The exposure concentration series were as follows: 2, 3, 5, 10, 20, 30, 50 and 100%.

The bioassays were conducted in 300-mL glass containers. The test volume was 50 mL. Each test vessel contained ten daphnids. Each test was accompanied by a control which was subjected to the same test conditions as the effluent concentrations.

All tests were conducted at a temperature of 21 ± 1C° under a control light regime (12 hours light/12 hours darkness).

Dissolved oxygen, pH, temperature and conductivity were recorded prior to and after bioassay duration. *Daphnia* immobilization and mortality was recorded at 24 and 48 hours, and the 48-hour median lethal concentrations (48-h LC_{50}) values and 95% confidence limits were determined by moving average method (13).

3 RESULTS

This section presents the results of the experimental program to characterize the physical, chemical and leaching properties of the AFBC residue samples. The complete analytical results are presented in Appendix A.

3.1 Physical Characteristics

3.1.1 Specific Gravity. The range of specific gravities for single particles determined for each type of AFBC residue evaluated are:

Residue Type	Median Value	Range
bed material	2.75	2.58 to 2.82
cyclone material	2.71	2.44 to 2.83
baghouse material	2.50	2.08 to 2.77

Very little variation in specific gravity was found either between similar residues or residue types. All samples ranged between 2.08 and 2.82 which are typical of soils.

3.1.2 Minimum Density. The results of the minimum density determinations for the as received residues are:

Residue Type	Median Value (Mg/m^3)	Range (Mg/m^3)
bed material	1.467	1.250 to 1.615
cyclone material	0.949	0.562 to 1.322
baghouse material	0.611	0.257 to 0.951

The bed materials had the greatest minimum densities followed by the cyclone and baghouse materials, respectively. The baghouse residues achieved less than half the minimum densities compared with the bed residues. This is likely due to the more uniform smaller particle size distributions for this waste type.

3.1.3 Particle Size. Particle size distributions for all AFBC residues are shown in Figure 2. The seven bed materials were composed of particles of a wide range of sizes, from 10 to 0.01 mm, and were classified as poorly sorted coarse sand. The D_{50} particle size was 0.5 mm. A pronounced change in the shape of the curve was evident at the 400 sieve size particle range. Above this particle size sieves were used to determine particle size while below a hydrometer procedure was used.

The residues from the cyclone materials were finer and more closely graded compared to the bed materials and were classified as medium sand. The particles ranged from 1.0 to 0.05 mm with a D_{50} of 0.05 mm. A less pronounced change in the curve shape was evident for particles around 400 sieve size.

The particles of the baghouse materials ranged from 0.05 to 0.01 mm in size, were closely sorted and were considered to be silt-sized particles. The D_{50} of this type of residues was about 0.01 mm.

Many of the bed and cyclone material samples showed an increase in the percent finer particles from the 75 to 45 µm size classes. The particle size testing was repeated using larger sample sizes without the use of sodium hexametaphosphate. The increase in the particles was still evident. This increase is inconsistent with normal soil particle size distributions and is attributed to decrepitation of particles during the hydrometer testing.

3.1.4 Moisture Content. The moisture content of each sample was determined. The low moisture contents of the bed and cyclone materials would suggest that the samples had been properly stored and hydration of the residues had not occurred. All the bed and cyclone materials gained weight during the test procedure. This would be expected for samples containing readily hydrated compounds such as calcium oxide or sulphate. This will be discussed more fully in Section 4.2.

In terms of the baghouse materials, moisture content ranged between 0.3 and 26.0% (see Appendix A). Values up to several percent might be expected. However, the integrity of sample storage where moisture contents of 6.3% and 25% (S-BH-5 and S-BH-2) were found would be questioned.

3.2 Chemical Characteristics

The chemical characteristics of the residues were determined by analyzing their trace chemical, crystalline and exothermic properties. The results of this testing follow.

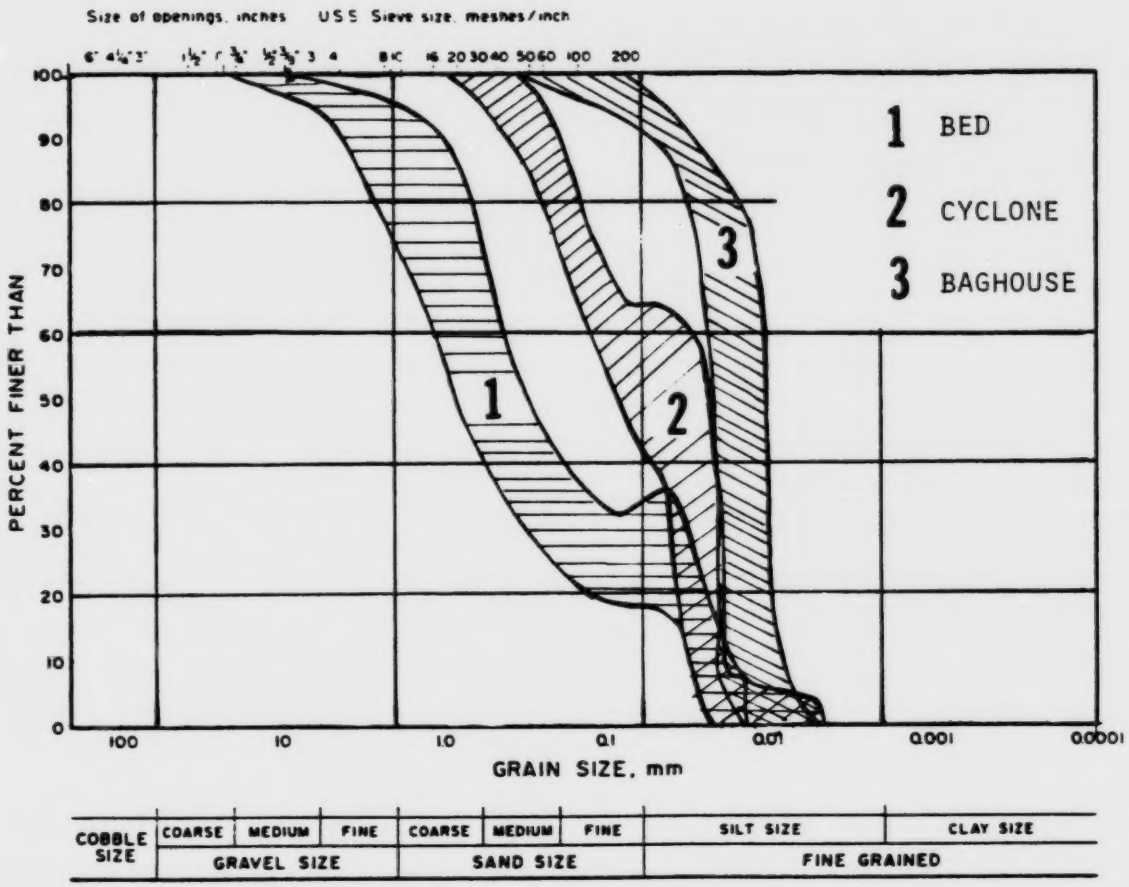

FIGURE 2 AFBC RESIDUE PARTICLE SIZE DISTRIBUTIONS

3.2.1 Trace Chemical Composition. The trace chemical composition of the combustion residues is dependent upon fuel and sorbent used during the combustion test and the partitioning of the elements between the bed, cyclone and baghouse materials. The ranges of the main chemical constituents among the three residue types, which are typically present in concentrations greater than 0.05%, are summarized in Table 2.

The residues were principally composed of the metals calcium, aluminum and iron with lesser portions of magnesium, sodium, manganese, titanium, lead, nickel, vanadium and zinc.

Wide variations were observed for selected parameters for some of the different residue types. For example, the manganese content of the bed materials ranged from 103 to 2100 mg/kg, the vanadium content of cyclone materials from 20.7 to 2770 mg/kg while the lead content ranged from 10 to 980 mg/kg in the baghouse materials. This variation between residue compositions is attributed to the different compositions of the fuel and sorbent used in each combustion run and, to a lesser extent, the combustor operating conditions. In the cases of vanadium, nickel, and molybdenum, the highest residue concentrations were found where petroleum coke was used as the combustor fuel. These large concentrations widened the range of concentrations encountered in the residues.

A comparison between the chemical composition ranges among the three residue types shows that greatest calcium and aluminum concentrations are likely in the bed materials while the iron, nickel, sodium, vanadium and zinc concentrations are highest in the baghouse material. The partitioning of these metals into the baghouse is important since this residue type represents a significant volume of AFBC waste to be disposed of and many of these metals are of environmental concern. If sufficiently mobilized from the residue, they could adversely affect receiving waters.

3.2.2 Crystalline Composition. The crystalline composition of the residues was determined in order to determine the form in which the quantified elements would be present. Such analyses identify chemical compounds which may require special consideration for disposal.

The ranges of concentration of principal crystalline species present in the three AFBC residue types are summarized in Table 3. For the bed material, the main crystalline components were $CaSO_4$ and CaO and occasionally silica and silicates. Negative loss-on-ignition (LOI) values were found for some samples. This corresponds to a

TABLE 2 CHEMICAL COMPOSITION OF AFBC RESIDUES

Parameter	Material (mg/kg)		
	Bed	Cyclone	Baghouse
Aluminum	8 340 to 85 600	7 830 to 32 500	41 100 to 69 900
Calcium	178 000 to 364 000	125 000 to 331 000	92 100 to 292 000
Iron	11 700 to 34 100	17 300 to 70 800	22 300 to 218 000
Lead	<5 to 355	5 to 100	10 to 980
Magnesium	4 160 to 7 770	3 870 to 10 400	2 190 to 10 100
Manganese	103 to 2 100	108 to 1 950	620 to 1 720
Nickel	22 to 260	19 to 1 060	59 to 1 970
Sodium	500 to 7 200	200 to 2 100	2 800 to 7 400
Titanium	504 to 2 990	358 to 3 340	1 920 to 4 710
Vanadium	19.3 to 613	20.7 to 2 720	84.2 to 4 320
Zinc	14 to 53	56 to 555	93 to 1 110

TABLE 3 CRYSTALLINE COMPOSITION OF AFBC RESIDUE TYPES

Crystalline Compound	Material (%)		
	Bed	Cyclone	Baghouse
$CaSO_4$	11.17 to 42.94	7.26 to 19.23	13.89 to 24.36
CaS	nil to 2.92	0.11 to 1.76	0.49 to 3.01
$CaCO_3$	nil to 11.08	0.10 to 19.55	2.12 to 14.25
$Ca_3(PO_4)_2$	0.13 to 1.01	0.13 to 0.74	0.24 to 2.16
CaO (free)	22.19 to 39.54	17.26 to 45.39	0.95 to 28.32
Fe_2O_3	1.80 to 3.90	2.92 to 12.40	3.30 to 29.60
LOI	-2.57 to 2.33	8.24 to 44.23	0.86 to 31.56
Others (mainly SiO_2 and silicates)	9.2 to 52.92	10.50 to 28.73	25.54 to 40.05

weight gain during testing and is expected for residues containing large amounts of $CaSO_4$ which readily hydrate.

For the cyclone materials, the main crystalline components were CaO, $CaSO_4$, silica and silicates. High values of LOI for this residue type would be associated with unburned carbon particles captured in the cyclone. The $CaCO_3$ content of this type of residue ranged up to 19.55 percent which would also contribute to the loss on ignition.

The baghouse residues mainly contained $CaSO_4$, SiO_2 and silicates, and Fe_2O_3, and showed high LOI. The high concentration of SiO_2 and silicates is attributed to the presence of fine particles derived from clay in the limestone sorbent or shale in the coal fuel while the LOI probably represents finer unburned carbon particles. This type of residue also contained up to 14.25 percent of $CaCO_3$. As with the cyclone residue the carbonate in the baghouse material would degrade to CO_2 during the determination, thus contributing to the loss on ignition.

Comparing the three residue types, the bed material usually contained the largest $CaSO_4$ and least Fe_2O_3 and $CaCO_3$ composition. The cyclone materials contained the largest portions of CaO and $CaCO_3$ and showed the greatest loss-on-ignition, while the baghouse materials had the greatest CaS, $Ca_3(PO_4)_2$ and Fe_2O_3 components.

Two crystalline components which would require special consideration in a waste disposal situation are CaO and CaS. Calcium oxide would be expected to contribute to the exothermicity of the wastes. Almost all samples contained considerable portions, up to 45 % in some cyclone materials. Likewise, almost all samples contained some CaS. The maximum concentration observed was 3.01 % in a baghouse material sample. Calcium sulphide, when contacted with acid, would produce hydrogen sulphide gas.

3.2.3 Exothermic Characterization. The heat release on contact with water or exothermicity of the AFBC residues are summarized in the following. The rise in temperature of the water and residue mixture and the calculated heat release are presented.

Residue Type	Rise in Temperature (°C)	Heat Release (kJ/kg)
bed material	2 to 11	46.8 to 257.6
cyclone material	1.5 to 19	35.1 to 444.9
baghouse material	0 to 11	0 to 257.6

The largest rises in temperature (up to 19°C) were found for the cyclone materials. The rises for the bed and baghouse material were in a similar range of 0 to 11°C. Although a heat release of 445 kJ/kg was found for a cyclone material, the range of 50 to 250 kJ/kg was typical for the AFBC residues.

3.3 Leachate Characteristics

The AFBC residues were subjected to the WTC leach test procedure in order to predict the mobilization of chemical species from the waste in an unconditioned, uncompacted state, in a disposal situation. Leachates produced by the laboratory-scale testing were subsequently aerated to predict the effect of contact with the atmosphere on the leachate chemical characteristics. The aeration experiments were conducted at various mixing energies to simulate a range of possible treatment designs involving mechanical aeration.

The Langlier Scaling Indices were calculated in order to predict the scale-forming potential of the untreated and treated leachates.

The computerized chemical equilibrium program PHREEQE was assessed as a tool to predict the leachability of the residues and the effect of atmospheric contact on leachate chemistry using only minimal data inputs.

3.3.1 Leachate Composition. The ranges of the main chemical constituents for the laboratory-scale produced leachates from the three AFBC residue types are summarized in Table 4. With the exception of two baghouse material leachates, all were very alkaline with typical pH values greater than 12. This accounts for the very low concentrations of metals in the leachates. The leachates had very high dissolved solids contents, usually greater than 5000 mg/L. These were composed of dissolved inorganic species; however, measurable concentrations of total organic carbon (TOC) in the 2.0 to 52 mg/L range were also found.

The leachates from the bed material were mainly composed of dissolved calcium, sulphate and, occasionally, potassium. Other cations such as barium, molybdenum, sodium and strontium and the anions, chloride and fluoride were also quantified at concentrations greater than 1.0 mg/L. For the cyclone materials, leachates were also primarily composed of calcium and sulphate with lesser concentrations of the other parameters. In the case of the baghouse material leachates, greater variations in leachate composition were apparent. A wider range in pH (8.1 to 12.3) and TDS (3970 to 7220 mg/L) was found, although the principal dissolved species were still calcium and sulphate.

TABLE 4 LEACHATE CHEMICAL COMPOSITION FOR AFBC RESIDUES

Parameter	Material		
	Bed	Cyclone	Baghouse
pH	12.2 to 12.5	12.2 to 12.5	8.1 to 12.3
TDS	4450 to 4790	4300 to 5010	3970 to 7220
Barium	0.070 to 2.76	0.0147 to 0.776	0.030 to 0.513
Calcium	1320 to 1590	1220 to 1730	908 to 1540
Chloride	1.50 to 15.5	1.08 to 108	76.2 to 1820
Fluoride	< 0.5 to 1.8	< 0.5 to 2.4	< 0.5 to 8.6
Molybdenum	0.3 to 5.2	0.3 to 1.0	0.3 to 1.2
Potassium	< 1 to 479	< 1 to 30	< 1 to 69
Sodium	< 1 to 50	< 1 to 15	< 1 to 35
Strontium	2.31 to 4.28	1.42 to 2.27	1.04 to 3.06
Sulphate	1140 to 1720	1230 to 1800	1100 to 1790
TOC	1.5 to 30	2.0 to 40	2.0 to 52

Note: All analyses expressed in mg/L except pH.

In comparison with the other waste types, this residue type produced leachates with greater concentrations of chloride and fluoride.

3.3.2 Aeration Experiments. The aeration experiments were conducted for a minimum of 19 hours until the pH of the leachate appeared to have stabilized. There was one exception of a baghouse material which required only three hours to achieve the expected pH. The sample was mixed at 195 rpm, which, based on the geometry of the test equipment, would provide a "G" value of 430 s^{-1}. This is typical of a rapid-mix condition.

Figure 3 shows a typical neutralization curve from the aeration tests (Test Run No. 1-baghouse material). The pH gradually decreased over a period of between 10 and 13 hours when a sudden drop in pH was observed. This is referred to as the midpoint of the curve and roughly corresponds to the presence of equal portions of carbonate and bicarbonate alkalinity. With continued aeration, a more gradual drop in pH was observed for the remainder of the tests until a pH of about 8.3 was reached. At this point, all alkalinity is present as bicarbonate with no H_2CO_3 or carbonate present.

The pH was reduced from an initial value of about 12.5 to a final value of about 8.0. The solids which were formed as a result of the reactions usually settled slowly producing a clear supernatant. The sludge volumes were less than 0.5 % and usually 0.2 %. A reduction in sample volume of about 30 % was observed following the aeration tests and this was attributed to evaporation due to the agitation. To permit comparison of the before and after aeration leachate chemical composition, the analytical results were adjusted to consider this evaporative loss.

The ranges in concentration of the untreated and treated (aerated) AFBC residue leachates are compared in Table 5. The results from the three types of residues are combined since they show similar trends. Data from one baghouse material which had a leachate with an unusually low initial pH has been excluded from this table.

Aeration reduced the pH, alkalinity, hardness, TDS and concentrations of aluminum and calcium by large amounts, and sulphate was also reduced, but to a lesser degree. Other parameters were present in very low concentrations or were not significantly affected by aeration.

In several cases, slight increases in the concentrations of a few parameters were observed but these are attributed to analytical difficulties in quantifying parameters present in low concentrations in a high TDS background, and are not considered significant.

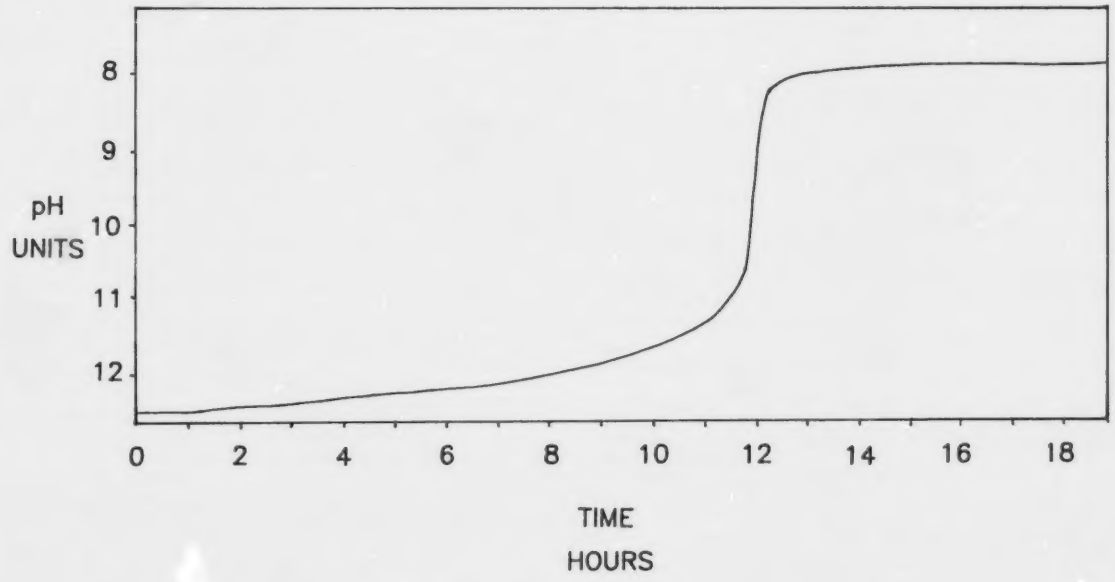

FIGURE 3 TYPICAL NEUTRALIZATION CURVE

TABLE 5 COMPARISON OF UNTREATED AND TREATED AFBC LEACHATES

Parameter	Range of Untreated Concentrations	Range of Treated* Concentrations
pH	12.3 to 12.5	7.7 to 7.8
Alkalinity	1720 to 2600	38 to 60
Hardness	3230 to 4325	807 to 2510
TDS	4450 to 6830	1600 to 3530
Aluminum	<0.05 to 15.2	<0.01
Calcium	1290 to 1730	323 to 1000
Sulphate	1230 to 1700	970 to 1490

Note: All results expressed in mg/L except pH.
* Leachates treated by aeration.

Samples of the precipitated solids were chemically analyzed using XRD and AA to identify their chemical composition. The solids were composed of $CaCO_3$ (72 to 86%), $CaSO_4$ (9.5 to 21.8%) and $Ca(OH)_2$ (1.1 to 17.8%).

3.4.3 Effect of Mixing Regime on Reaction. The effect of the rate of agitation on the aeration reaction was investigated by aerating one leachate sample under four different mixing regimes. The previously described experimental apparatus was used for all tests except that the rate of mechanical agitation was varied to provide a range of "G" values.

The conditions used to provide the various agitations which are representative of a wide range of conditions encountered in wastewater treatment were:

Test Run	Mixing (rpm)	G (s^{-1})
1	0	110
2	195	430
3	450	1500
4	560	2080

In all cases, the initial and final pH were the same regardless of mixing conditions. As well, the settling rate of formed solids and the supernatant were the same. Figure 4 shows the neutralization curves for the aeration experiments conducted at the four mixing conditions.

A comparison of the chemical composition of the aerated leachates shows that rate of mixing had no effect on the composition of the treated samples. Likewise, the precipitated solids were very similar, primarly composed of $CaCO_3$ and $CaSO_4$. The only difference observed was the length of time required to achieve the final pH of around 8. A twenty-fold increase in mixing reduced the reaction time by almost 50 %.

The Langlier Indices for the untreated leachates indicate a strong tendency to scale. The treated leachates also showed a tendency to scale but to a lesser extent. The limitations of the use of this scaling index are discussed in Section 4.2.2.

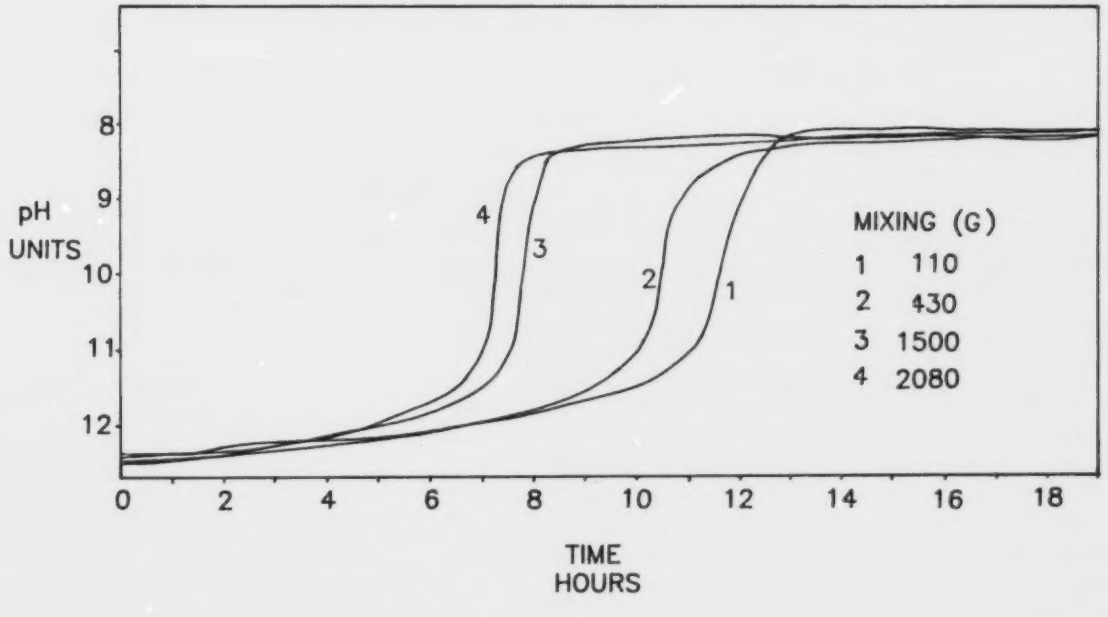

FIGURE 4 EFFECT OF MIXING ON NEUTRALIZATION CURVE

3.3.4 Results of Computerized Predictions. The output listing from the program PHREEQE, shown in Appendix B, contains two separate simulations. The first simulation (section 1) shows the characteristics of the distilled water (solution number 1), and then adds the "reaction" (step number 1) that is made up of the concentration of all nine constituents derived from the analysis of the ash solids. This step produces the "Total Molalities of Elements" as dissolved from the reaction, and a "Look Min" listing of mineral saturation status. A second listing of "Total Molalities of Elements" is then given, but since no precipitation or dissolution of mineral phases was allowed in this step, there is no difference between the two listings of "Total Molalities". Finally, a "description of the solution" after the reaction is given, followed by a detailed listing of all dissolved species in the solution ("Distribution of Species").

The second simulation begins with a restating of the "imposed mineral constraints on reaction solution". This result of the second simulation begins with the "Total Molalities of Elements" in the starting solution, which in this case is the product of the first simulation (i.e., distilled water plus unconstrained reaction). The next section of output is called "Phase Boundaries", which shows the amount (in moles) of each of the specified mineral phases that is dissolved (positive "delta phase") or precipitated (negative delta phase) in order to produce conditions of saturation with respect to the mineral phase. The "Look Min" table that follows next shows the final mineral saturation status after the precipitation/dissolution of the specified mineral phases. If the simulation has been conducted correctly, all of the saturation index values (Log/IAP/KT) in this table will be either zero or negative (with the possible exceptions of quartz and chalcedony), indicating no phases remain supersaturated. Next is listed the "Total Molality of Elements" in the final solution, after mineral precipitation/dissolution. This is followed with " Description of Solution" and "Distribution of Species", both of which refer to the final solution of the simulation.

This pair of simulations is then followed by an analogous pair of simulations corresponding to open-system conditions.

The results of the PHREEQE simulations of leachate chemistry for the nine test samples are presented in Table 6. For each sample two conditions are simulated (i.e., closed and open with respect to CO_2).

The results shown in Table 6 highlight the differences between the open- and closed-system conditions. Concentrations of total dissolved solids (TDS) for the closed-system simulations are typically 4000 to 5400 mg/L, with pH values between 12 and 13. In

TABLE 6 SUMMARY OF RESULTS - PHREEQE LEACH TEST SIMULATIONS FOR CLOSED SYSTEM (CO_2) AND OPEN SYSTEM (atmospheric PCO_2) TRIALS

Sample	Conditions**	Concentration (mg/L)												
		Ca^{2+}	Fe	SiO^2	CO_3^{2-}	HCO_3^-	SO_4^{2-}	PO_4^{3-}	$H_2PO_4^-$	K	Al	TDS[1]	TDS[2]	pH
S-B-1	No CO_2	2239	0.0	640.6	0.0	0.3	988.0	0.0	0.0	139.0	95.9	4790	4103	12.66
S-B-1	Atm CO_2	816.4	0.0	0.0	0.0	19.8	1129	0.0	0.0	0.0	0.0	-	1966	7.67
S-C-1	No CO_2	2401	0.0	616.2	0.0	0.3	953.3	0.0	0.0	133.7	92.2	4860	4197	12.64
S-C-1	Atm CO_2	983.8	0.0	0.0	0.0	18.3	1026	0.0	0.0	0.0	0.0	-	2029	7.63
S-BH-1	No CO_2	2458	0.0	608.6	0.0	0.3	942.6	0.0	0.0	132.0	91.1	4887	4232	12.63
S-BH-1	Atm CO_2	1044	0.0	0.0	0.0	17.9	1000.0	0.0	0.0	0.0	0.0	-	2062	7.61
S-B-5	No CO_2	2548	0.0	597.1	0.0	0.3	926.8	0.0	0.0	129.5	89.4	4934	4291	12.62
S-B-5	Atm CO_2	1142	0.0	0.0	0.0	17.4	964.5	0.0	0.0	0.0	0.0	-	2124	7.60
S-C-5	No CO_2	3222	0.0	533.1	0.0	0.3	842.8	0.0	0.0	115.6	79.8	5368	4793	12.57
S-C-5	Atm CO_2	1876	0.0	0.0	0.0	15.2	829.8	0.0	0.0	0.0	0.0	-	2720	7.50
S-BH-5	No CO_2	1650	0.0	5189	0.0	0.3	1088	0.0	0.0	112.6	77.7	4032	3448	12.59
S-BH-5	Atm CO_2	602.5	0.0	0.0	0.0	23.2	1426	0.0	0.0	0.0	0.0	-	2052	7.76
S-B-8	No CO_2	2536	0.0	598.6	0.0	0.3	928.8	0.0	0.0	129.8	89.6	4927	4283	12.63
S-B-8	Atm CO_2	1129	0.0	0.0	0.0	17.5	968.8	0.0	0.0	0.0	0.0	-	2115	7.60
S-C-8	No CO_2	3053	0.0	546.4	0.0	0.3	859.6	0.0	0.0	118.5	81.8	5249	4660	12.58
S-C-8	Atm CO_2	1693	0.0	0.0	0.0	15.6	851.7	0.0	0.0	0.0	0.0	-	2560	7.52
S-BH-8	No CO_2	3215	0.0	533.6	0.0	0.3	843.4	0.0	0.0	115.7	79.9	5363	4788	12.57
S-BH-8	Atm CO_2	1869	0.0	0.0	0.0	15.2	830.6	0.0	0.0	0.0	0.0	-	2714	7.50

1 TDS including dissolved OH^-.
2 TDS not including dissolved OH^-.
* TDS includes 2097 mg/L dissolved H_2CO_3.
** 'No CO_2' refers to closed-system simulations; 'Atm CO_2' refers to open-system simulations.

contrast, the open system simulations show TDS concentrations of 1900 to 2800 mg/L, with pH in all cases between 7.5 and 7.8. Among individual constituents, SiO_2 displays the largest difference between the two conditions, reflecting the great solubility of potassium-feldspar at high pH, and consequent higher SiO_2 concentrations in the closed-system simulations. The concentration of Ca^{2+} is generally 1.7 to 2.7 times higher in the closed-system simulations, since under closed-system conditions virtually all of the available CO_2 has precipitated out in calcite, and only gypsum and $Ca(OH)^2$ remain to limit the amount of dissolved Ca^{2+}.

The simulated leachates are typically at saturation with respect to several mineral phases, notably gypsum ($CaSO_4 \cdot 2H_2O$), apatite ($Ca_5(PO_4)_3OH$) hematite (Fe_2O_3) and often calcite ($CaCO_3$).

From the PHREEQE simulations it is also possible to determine the amount of material that remains undissolved in a 20:1 suspension, as a result of mineral saturation constraints. That is, even at a 20:1 water-to-solid ratio, some of the soluble or sparingly soluble constituents of the ash remain in the solid phase because the solution reaches saturation with respect to various solid constituents. Table 7 shows the relative amount of each substance that is in solution ("Dissolved Phase") or remains in solid form ("Solids Phase"). To summarize the results in this table, in a 20:1 suspension $CaSO_4$ remains primarily in the solid phase, because the 20:1 solution is saturated with respect to gypsum ($CaSO_4 \cdot 2H_2O$) in all cases. Calcium sulphide is in all cases totally dissolved because of the oxidation of sulphide to sulphate. Nearly all of the original $CaCO_3$ is undissolved in the closed-system simulations; in the open-system simulations the amount of $CaCO_3$ precipitated exceeds the amount originally present because of the input of CO_2^- from atmospheric CO_2. Because of their low solubility, $Ca_3(PO_4)_2$ and Fe_2O_3 remain completely undissolved in all of the samples. In all but two of the closed-system simulations (S-BH-5 and S-BH-8 are the exceptions) a significant amount (56 to 88%) of the available CaO remains in the solid phase as precipitated $Ca(OH)_2$. In the open-system simulations all of the $Ca(OH)_2$ is dissolved.

3.4 Leachate Aquatic Toxicity and Genotoxicity Characterization

The complete test battery was applied to both treated (aerated) and untreated samples of Runs 5 and 8. The results are summarized in Table 8. In addition, the untreated samples from Runs 1, 2, 4, and 6 were analyzed by the Microtox™ procedure. These results are reported in Table 9. A section which shows the results of duplicate tests is included in Appendix C.

TABLE 7 PROPORTION OF TOTAL SOLUBLE COMPONENTS DISSOLVED AT 20:1 (Liquid:Solids)

Sample	Condition WRT PCO_2	Phase	Component Proportion (%) Dissolved vs Solid Phase					
			$CaSO_4$	CaS	$CaCO_3$	$Ca_3(PO_4)_2$	CaO	Fe_2O_3
S-B-1	No CO_2	dissolved	2.2	100.0	0.1	0.0	12.8	0.0
		solid	97.8	0.0	99.9	100.0	87.2	100.0
S-B-1	Atm CO_2	dissolved	2.8	100.0	-	0.0	100.0	0.0
		solid	97.2	0.0	-	100.0	0.0	100.0
S-C-1	No CO_2	dissolved	2.6	100.0	1.0	0.0	12.7	0.0
		solid	97.4	0.0	99.0	100.0	87.3	100.0
S-C-1	Atm CO_2	dissolved	4.2	100.0	-	0.0	100.0	0.0
		solid	95.8	0.0	-	100.0	0.0	100.0
S-BH-1	No CO_2	dissolved	0.0	100.0	0.1	0.0	21.5	0.0
		solid	108.2	0.0	99.9	100.0	79.5	100.0
S-BH-1	Atm CO_2	dissolved	0.0	100.0	-	0.0	100.0	0.0
		solid	107.5	0.0	-	100.0	0.0	100.0
S-B-5	No CO_2	dissolved	0.0	100.0	0.0	0.0	27.3	0.0
		solid	100.4	0.0	100.0	100.0	72.7	100.0
S-B-5	Atm CO_2	dissolved	0.0	100.0	-	0.0	100.0	0.0
		solid	100.1	0.0	-	100.0	0.0	100.0
S-C-5	No CO_2	dissolved	15.1	100.0	0.0	0.0	22.6	0.0
		solid	84.9	0.0	100.0	100.0	77.4	100.0
S-C-5	Atm CO_2	dissolved	14.8	100.0	-	0.0	100.0	0.0
		solid	85.2	0.0	-	100.0	0.0	100.0
S-BH-5	No CO_2	dissolved	12.4	100.0	0.1	0.0	100.0	-
		solid	87.6	0.0	99.9	100.0	0.0	-
S-BH-5	Atm CO_2	dissolved	18.3	100.0	-	0.0	100.0	-
		solid	81.7	0.0	-	100.0	0.0	-
S-B-8	No CO_2	dissolved	0.0	100.0	0.0	0.0	27.1	0.0
		solid	106.5	0.0	100.0	100.0	72.9	100.0
S-B-8	Atm CO_2	dissolved	0.0	100.0	-	0.0	100.0	0.0
		solid	105.5	0.0	-	100.0	0.0	100.0
S-C-8	No CO_2	dissolved	24.2	100.0	0.0	0.0	43.7	0.0
		solid	75.8	0.0	100.0	100.0	56.3	100.0
S-C-8	Atm CO_2	dissolved	23.9	100.0	-	0.0	100.0	0.0
		solid	76.1	0.0	-	100.0	0.0	100.0
S-BH-8	No CO_2	dissolved	0.3	100.0	0.0	0.0	97.7	0.0
		solid	99.7	0.0	100.0	100.0	2.3	100.0
S-BH-8	Atm CO_2	dissolved	0.0	100.0	-	0.0	100.0	0.0
		solid	100.0	0.0	-	100.0	0.0	100.0

TABLE 8 RESULTS OF AQUATIC TOXICITY AND GENOTOXICITY TESTS ON LEACHATES FROM AFBC WASTES

	Run No. 5		Run No. 8	
	Untreated	Treated	Untreated	Treated
A) BED SAMPLES[1,2]				
(a) Microtox™: (i) 5-min EC_{50}	0.66% (0.60 to 0.73%)	Not toxic[3]	0.73% (0.67 to 0.80%)	Not Toxic[3]
(ii) 15-min EC_{50}	0.63% (0.56 to 0.71%)	Not toxic[3]	0.67% (0.61 to 0.73%)	Not toxic[3]
(b) *Selenastrum capricornutum*: Growth Inhibition 96-h EC_{50}	20% [11 to 46%]	Not toxic	20% 11 to 46%	Not toxic
(c) *Daphnia magna*: 48-h LC_{50}	1.8% (1.28 to 2.31%)	71% [50 to 100%]	7.8% (6.13 to 10.0%)	71% [50 to 100%]
(d) SOS Chromotest™: SOS-DNA repair induction threshold	Not Genotoxic	Not Genotoxic	Not Genotoxic	Not Genotoxic
Note[4]: Dilution to give pH 6-7	2.5%	-	2%	-
Dilution to give pH 9-10	10%	-	20%	-
B) CYCLONE SAMPLES[1,2]				
(a) Microtox™: (i) 5-min EC_{50}	0.75% (0.66 to 0.84%)	Not toxic	0.94% (0.80 to 1.10%)	Not toxic
(ii) 15-min EC_{50}	0.71% (0.62 to 0.82%)	Not toxic	0.88% (0.74 to 1.0)	Not toxic
(b) *Selanastrum capricornutum*: Growth Inhibition 96-h EC_{50}	30% [23 to 91%]	Not toxic	30% [23 to 91%]	Not toxic
(c) *Daphnia magna*: 48-h LC_{50}	6.4% (5.0 to 8.7%)	66% [54 to 81%]	1.8% (1.3 to 2.4%)	84% (76 to 93%)
(d) SOS Chromotest™: SOS-DNA repair induction threshold	Not Genotoxic	Not Genotoxic	Not Genotoxic	Not Genotoxic
Note[4]: Dilution to give pH 6-7	1%	-	2%	-
Dilution to give pH 9-10	25%	-	25%	-
C) BAGHOUSE SAMPLES[1,2]				
(a) Microtox™: (i) 5-min EC_{50}	Not toxic	Not toxic	0.83% (0.67 to 0.91%)	Not toxic
(ii) 15-min EC_{50}	Not toxic	Not toxic	0.78% (0.72 to 0.96%)	Not toxic
(b) *Selenastrum capricornutum*: Growth Inhibition 96-h EC_{50}	30% [23 to 91%]	Not toxic	10% [5.6 to 23%]	Not toxic
(c) *Daphnia magna*: 48-h LC_{50}	42% (32 to 58%)	71% (50 to 100%)	2.7% (2.4 to 3.5%)	62% (49 to 79%)
(d) SOS Chromotest™: SOS-DNA repair induction threshold	Not Genotoxic	Not Genotoxic	Not Genotoxic	Not genotoxic
Note[4]: Dilution to give pH 6-7	None	-	2%	-
Dilution to give pH 9-10	None	-	40%	-

Results expressed as % volume/volume, ( ) 95% confidence limits.

1. - Microtox™ EC_{50} indicates the percent sample volume (v/v) which caused a 50% reduction in light (linked to cell respiration) produced by the luminescent bacterium *Photobacterium phosphoreum*.
   - *Selenastrum capricornutum* EC_{50} indicates the % sample (v/v) which caused a 50% inhibition in growth during 96-hours.
   - *Daphnia magna* LC_{50} indicates the % sample volume (v/v) caused a 50% mortality rate after an exposure period of 48 hours.
   - The SOS Chromotest™ procedure provides the threshold sample concentration which causes induction of the SOS DNA repair genes in a genetically engineered strain of *E. coli*.
   - Using the established protocols, testing full strength samples can only be achieved when determining *Daphnia* LC_{50}'s. When *Daphnia* are tested, they are individually removed from their culture dilution water, and placed directly into the test sample, thereby causing insignificant sample dilution. When microorganisms are tested, they are introduced into the sample in an aqueous suspension and dilute the sample. Thus the maximum concentration of sample which can be tested is 45.5%, 91%, and 9.1% for Microtox™ EC_{50}, *Selenastrum capricornutum* EC_{50}, and SOS Chromotest™, respectively.
2. In brackets below each toxicity result are 95% confidence limits. In the case of the algal assays and some of the *Daphnia* tests, inadequate data were available to provide 95% confidence limits. When this occurred, the numbers in brackets are the intervals of sample concentration between which no effect (0% growth inhibition) and total (100% growth inhibition) effect were observed. These intervals are indicated by square brackets.
3. These leachates, when neutralized by sulphuric acid, also appeared to be nontoxic to Microtox™ bacteria.
4. For comparison with Microtox™ and algal toxicity test EC_{50} results, the dilution of each sample required to change its pH to pH 6-7 and to pH 9-10 (pH ranges not toxic to Microtox™ bacteria and *Selenastrum capricornutum*, respectively) is presented. This comparison can provide insight on the contribution of a sample's pH to its total toxic effect on these organisms.

TABLE 9 RESULTS OF MICROTOX™ TESTS ON UNTREATED LEACHATES FROM AFBC WASTES[1,2]

Sample Types Characterized		5-minute EC_{50}	15-minute EC_{50}
Bed Samples	Run 1	1.4 (1.1 to 1.8)	1.3 (0.98 to 1.7)
	Run 2	0.88 (0.68 to 1.1)	0.79 (0.74 to 0.83)
	Run 4	0.70 (0.59 to 0.83)	0.67 (0.62 to 0.72)
	Run 5	0.66 (0.60 to 0.73)	0.63 (0.56 to 0.71)
	Run 6	0.65 (0.60 to 0.69)	0.61 (0.58 to 0.65)
	Run 8	0.73 (0.67 to 0.80)	0.67 (0.61 to 0.73)
Cyclone Samples	Run 1	0.65 (0.53 to 0.80)	0.51 (0.45 to 0.58)
	Run 2	0.71 (0.66 to 0.78)	0.69 (0.63 to 0.75)
	Run 4	0.78 (0.67 to 0.92)	0.77 (0.70 to 0.84)
	Run 5	0.75 (0.66 to 0.84)	0.71 (0.62 to 0.82)
	Run 6	0.60 (0.54 to 0.67)	0.57 (0.51 to 0.64)
	Run 8	0.94 (0.8 to 1.1)	0.88 (0.74 to 1.0)
Baghouse Samples	Run 1	0.75 (0.60 to 0.94)	0.74 (0.61 to 0.90)
	Run 2	Not toxic	Not toxic
	Run 4	4.6 (4.2 to 5.0)	4.4 (4.0 to 4.8)
	Run 5	Not toxic	Not toxic
	Run 6	3.4 (3.1 to 3.9)	3.2 (2.8 to 3.6)
	Run 8	0.83 (0.67 to 0.91)	0.78 (0.72 to 0.96)

1. Microtox™ EC_{50} indicates the percent sample concentration which caused a 50% reduction in light (linked to cell respiration) produced by the luminescent bacterium *Photobacterium phosphoreum*. The maximum concentration of sample which can be tested is 45.5%.

2. Results expressed as % volume/volume, ( ) = 95% confidence limits.

3.4.1 Microtox™ Toxicity Assay. By reviewing Table 8, it can be seen that, with the exception of the baghouse samples in Run 5, the EC_{50} values of untreated leachates from Runs 5 and 8 were lower for Microtox™ bacteria than the EC_{50}'s for the algal toxicity assays and the LC_{50}'s of the *Daphnia magna* toxicity assay. Most of the Microtox™ EC_{50} results (Tables 8 and 9) were similar, falling into a range of 0.51% to 1.4% sample volume. However, leachate samples from Runs 2, 4, 5, and 6 of the baghouse samples appeared to be less toxic. Baghouse Run 5 leachate samples appeared to be non-toxic to the Microtox™ bacteria (i.e., EC_{50} of 50%).

Following aeration treatment of leachates from Runs 5 and 8, no toxicity to Microtox™ bacteria was detected. In order to investigate the effect of using acids to neutralize the leachates, the toxicity of bed samples from Runs 5 and 8, following neutralization with sulphuric acid, was also examined. Again, no measurable toxic response was observed. This indicates that the use of sulphuric acid in place of aeration to reduce the leachate pH does not change the measured toxic response when the Microtox™ procedure is used.

3.4.2 Algal Toxicity Assays. The 4-day growth-inhibition EC_{50} values for *Selenastrum capricornutum* ranged from 12 to 23% sample volume. Baghouse Run 5 leachate had an EC_{50} of 30%. This was the only case where an algal EC_{50} value was lower than the Microtox™ EC_{50} and the *Daphnia magna* LC_{50}.

As occurred with the Microtox™ tests, no toxic effect was observed with the algal assays when the leachates had undergone aeration treatment.

3.4.3 SOS Chromotest™ Genotoxicity Assay. All untreated and treated leachate samples tested up to a maximum concentration of 9.1% by volume (i.e., highest exposure possible without pre-concentration step) were non-genotoxic using the SOS Chromotest™. In addition, toxicity, as measured through the growth inhibition component of the test, was not observed in the 9.1% concentration.

3.4.4 *Daphnia magna* Toxicity Assay. With the exception of the Run 5 baghouse sample leachate, the 48-hour acute lethality LC_{50} values for untreated samples were within a similar range of toxicity (i.e., 1.8 to 7.8% LC_{50}). The Run 5 baghouse sample had an LC_{50} of 48%.

Following aeration treatment, it was possible to measure a toxic response to *Daphnia magna* where the Microtox™ and algae tests did not detect an effect. The greatest *Daphnia* toxic response was observed with the Run 8 baghouse sample which had a LC_{50} of 62%.

4 DISCUSSION

The results obtained during the experimental program are discussed in this section. Emphasis is placed on the environmental implications of the FBC waste characteristics with respect to their disposal and waste management alternatives.

4.1 Physical Characteristics

The physical characteristics of the AFBC residues will significantly affect the handling and disposal methods applicable to this type of combustion residue.

Each of the three residue types had a different particle size distribution range as shown in Figure 2. The particle size distribution data permit inferences to be made about the disposal and compactability of the residue. The bed materials were composed of widely varying size particles. This suggests that the waste would be easily compacted to obtain high densities and strengths. In contrast, the baghouse materials were very fine and uniformly sized. This type of residue would be more difficult to compact. To achieve high densities, greater compaction energies and water additions would be needed to permit particle reorientation. In a practical situation, the landfilled residue will be composed of a mixture of bed and baghouse materials which would vary depending on combustor operation. Therefore, without careful waste blending, a heterogenous waste would be produced which would require varying degrees of conditioning to achieve optimum strengths.

The particle size distributions indicate that the sieve and hydrometer test methods do not provide the same size data for the small particle component of the waste. This is particularly true for the bed and, to a lesser extent, the cyclone materials and is demonstrated by a step in the particle size distribution curves in the 200 sieve size. Previous investigations have attributed this to the decrepitation of particles because of expansion as a result of the reaction between water used in the hydrometer testing and the CaO content of the residue. This phenomenon was also observed during this study when kerosene was used in the hydrometer testing. One possible explanation is that the finer bed material and, to a lesser extent, cyclone residues are composed of aggregrates of finer particles which are not readily sieved but which break apart in a liquid medium.

The moisture contents of the residues were very low which is not unexpected since they are a result of a combustion process at 850°C. The residues would not be readily manageable due to their dustiness. The dry residue would not support vehicle traffic or be readily moved around at the disposal site using heavy equipment. A fugitive

dust emission problem would also exist at the site from wind-blown particle loss. Although the individual particles had soil-like densities, the bulk density of the waste would be low, particularly for the baghouse material, because of its small, uniform particle size.

The minimum densities achieved by the three residue types varied considerably. The baghouse materials had values averaging 0.611 Mg/m^3, while the bed material, on average, had values of 1.467 Mg/m^3. In comparison, fine sands typically have densities in the range of 1.6 to 1.8 Mg/m^3. These residues, therefore, would not produce a dense landfill without some form of conditioning or compaction.

The results of this test describe the densities of the residues which would be achieved without compaction or the addition of water. In a field situation, this would be analogous to dumping the residue out of a truck.

Although not addressed directly in the experimental program, residues of this type would require large additions of water for compaction and dust control purposes. In addition to the 15 to 20 % moisture typically added to control dust from PCF fly ash, additional water would be required to hydrate the CaO and $CaSO_4$ components of the waste. Water additions in the 40 to 50 % range might be expected for optimal conditions. If the residue conditioning was completed at the combustor, and not the disposal site, transportation costs would be expected to be much greater because of the increased weight from conditioning. Control over the water addition, however, might be better at the combustor ash handling facility than in a field situation at the disposal site.

4.2 Chemical Characterization

4.2.1 Crystalline Characterization. The results of the chemical characterizations confirm earlier investigations of pilot-scale AFBC wastes (1,2) which identified $CaSO_4$ and CaO as principal components of AFBC bed material, and CaO and compounds associated with LOI as major components of the cyclone materials. The CaO content of cyclone materials was up to 45%. Results from this study provide new data on the presence of CaS in bubbling AFBC pilot plant wastes. The CaS content of the baghouse materials was up to 3.0 %.

There was very little variation between the wastes produced from the various coals and limestones. The use of petroleum coke as a fuel did not greatly effect the waste chemical composition with the exception of nickel, molybdenum and vanadium which were present in concentrations much greater than in wastes from the combustion of coal.

The presence of CaO has been identified as a waste disposal concern because of the potential for heat release upon contact with water. In a landfilling situation, contact with water is inevitable and a resulting heat release might affect the integrity of liner materials and pose a hazard to disposal site workers. Figure 5 shows the relationship between CaO content of the bed and cyclone materials and the heat release. The relationship is not shown for the baghouse materials since no linear correlation between CaO and heat release was found for this residue type. Moisture content determinations indicated that the samples may not have been properly stored and they may have already been contacted by moisture, altering their exothermic behaviour.

The relationship between CaO content and heat release is apparently linear with regression coefficients of 0.92 and 0.90 for the cyclone and bed materials, respectively. The cyclone materials gave heat releases about one and one half times greater than the bed materials for similar CaO contents. Only the coal combustion residue data were included in the regression. The data from the petroleum coke combustion residue, shown using open symbols, was not included since it appears to be quite different. These samples have large a CaO content but unusually low heat releases. It is speculated that since the petroleum coke combustion tests were conducted at higher temperatures (1100°C compared to 850°C), the CaO particle porosity was changed making it less reactive with water because of its altered physical properties.

The heat releases of the bed and cyclone materials typically ranged between 50 and 250 kJ/kg. The heat releases of other similar materials when contacted with water are:

Material	kJ/kg	
CaO	1140	(14)
$CaSO_4$	126	(15)
ASTM Type I Cement	285	(16)
ASTM Type III Cement	348	(16)

Heat releases from the AFBC wastes were about one quarter of those associated with pure CaO and were typical of the hydration of gypsum and cements. This is not surprising since the wastes contained about 17 to 45 % CaO and were also composed of 7 to 42 % $CaSO_4$.

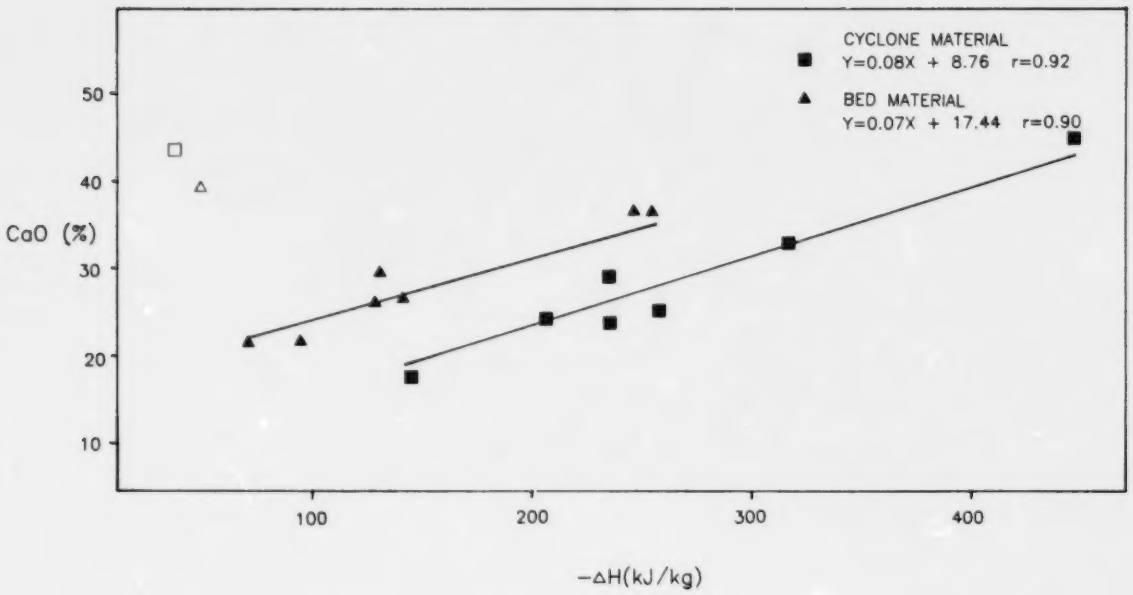

FIGURE 5 RELATIONSHIP BETWEEN CaO CONTENT AND HEAT RELEASE

The samples investigated during this study had exothermic properties similar to other materials routinely handled in industry such as gypsum or cement. This waste property, however, should still be addressed in disposal practice. The wastes did not exhibit the wide variation in this property identified in earlier investigations. This is attributed to the greater experience with the operation of the pilot plant combustor to obtain greater conversions of calcium to calcium sulphate through improved SO_2 gas capture.

Both the $CaSO_4$ and CaO, as mentioned earlier, would require large additions of water to fully hydrate the residues. Based on the following chemical reactions:

$$CaSO_4 + 2H_2O \longrightarrow CaSO_4 \cdot 2H_2O$$

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

Each mole of $CaSO_4$ would require two moles of water, while each mole of CaO would require one mole of water. This is the water requirement to chemically react the residue which must occur before water can be used to change the physical behaviour of the waste. This water addition of 30 to 35 % would be needed to hydrate the residue

before the 15 to 20 % water is added to allow particle reorientation during compaction. Although not investigated during this study, the rate of hydration reaction would be important in the development of waste handling practice and the day-to-day operation of a waste disposal system.

The presence of CaS in the bed material and baghouse residues suggests that reducing conditions occurred permitting its formation by the following reaction (17):

$$CaSO_4 + 2C \longrightarrow CaS + 2CO_2$$

There are other chemical reactions which produce CaS; however, this reaction seems most probable.

The presence of CaS may have important implications on waste disposal since H_2S gas can be formed when CaS is contacted by acid:

$$CaS + 2H^+ \longrightarrow Ca^{+2} + H_2S$$

The concentration of CaS does not appear to be large enough to cause a worker protection problem at the disposal site from the production of H_2S; however, there is a potential for production of unpleasant odours. Also, the utilization potential of the wastes may be limited due to the presence of CaS. Use of AFBC residues for acid neutralization may not be possible in uncontrolled situations.

Calcium carbonate was quantified in both the cyclone and baghouse materials at concentrations greater than those found in the bed material. The presence of $CaCO_3$ in the bed material may be expected, due to incomplete calcining of the limestone bed. The higher concentrations in the cyclone and baghouse materials are not readily explained. These data suggest that $CaCO_3$ may be forming by a reaction between fine CaO particles which escape the bed and CO_2 in the flue gases.

4.2.2 Leachate Characterization. The principal components of the leachates expressed as millequivalent per litre (meq/L) are shown in Figure 6. On this basis, the principal anionic components were sulphate and alkalinity with lesser portions of chloride and fluoride present. In terms of the cationic species, calcium was by far the major component with lesser amounts of potassium, aluminum, sodium and boron present. This leachate composition would be expected from a waste composed of readily soluble $CaSO_4$ and CaO. This distribution of dissolved species also helps explain the very low solubilities of metals and the precipitation of calcium carbonate and calcium sulphate during aeration.

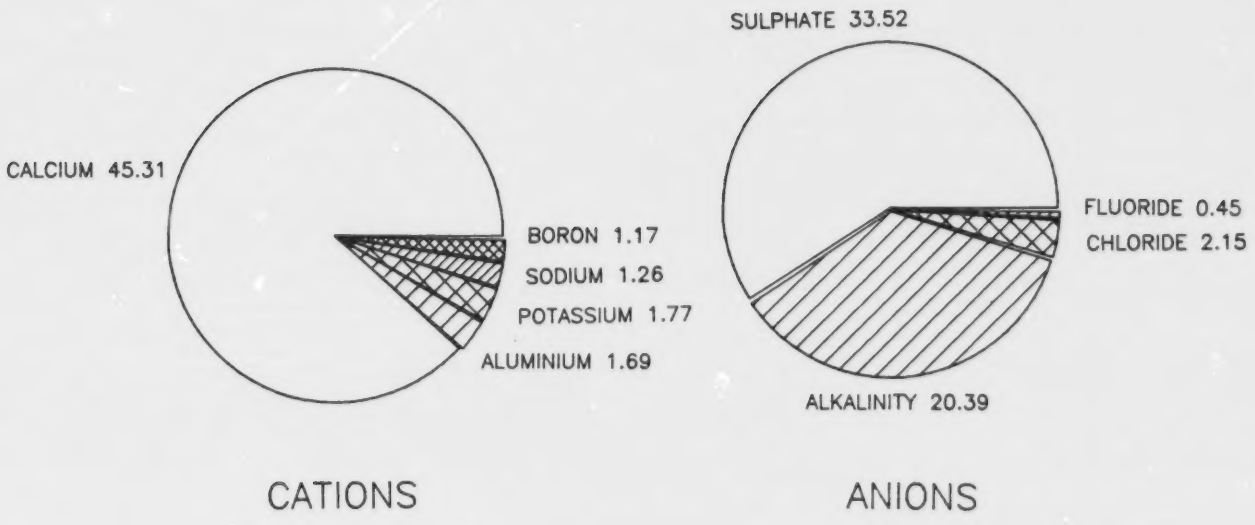

FIGURE 6 PRINCIPAL LEACHATE COMPONENTS (expressed as meq/L)

The TDS concentrations of the leachates ranged between 4000 and 7200 mg/L. Alkalinity, sulphate and calcium usually accounted for about three quarters of the total dissolved species.

An unexpected result of the leachate characterization was the quantification of dissolved organics in concentrations up to 52 mg/L. Organics passing through a combustion zone with temperatures in the 850°C range would not be expected to be soluble in water. The concentrations increase from the bed through cyclone and baghouse material leachates which suggests a relationship between gas temperature and the leachability of the organics. It is speculated that the water soluble organics may be formed within the flue gases as they cool.

The results of the QA/QC program are shown in Appendix A, Table A-12. A comparison of the results from the initial and second analyses of the leachate samples shows little variation. This indicates that the methods used for the chemical analyses were reproducible. The results from the analyses of the method blanks show that the constituents in the samples were a result of elements being leached and are not artifacts

of the leaching procedure. A small amount of contamination, slightly above the detection limit, was observed for calcium; however, this was not believed to be significant.

Investigations of the groundwater passing through the AFBC disposal site at Summerside, P.E.I., showed that the groundwater was only slightly affected by the disposed residue (18). The leachate characteristics predicted for the waste, using the same WTC method employed during this study, were quite different. Very high concentrations of calcium, sulphate, hardness and TDS were expected. The predicted leachability of the waste, therefore, was very dissimilar to the field behaviour of the wastes.

The differences between predicted leachate characteristics and the observed characteristics of groundwater are believed to be related to several limitations of the leaching protocol. Because waste is ground up prior to testing, the protocol does not account for the development (after placement) of low permeability and physical strength of the waste which would reduce the volume of leachate produced. Possible dilution of the leachate by groundwater is not addressed. The protocal is also limited in that interaction of atmospheric gases with leachate is not considered. The leaching protocol can therefore be considered to identify a worst case situation with respect to leachate characteristics and impact on groundwater.

The Langelier Index was calculated for the leachates in order to evaluate its use as a predictive tool. In all cases the leachates were found to have a potential to scale. The use of this scaling index is not believed to be reliable for alkaline wastewaters with chemistries like the leachates studied. The Quadratic Langelier Index could not be calculated using the graphical techniques originally described by Caldwell and Lawrence (19) due to the high alkalinities of the leachates. This method has recently been computerized but the necessary software is not yet readily available (20).

The use of the Langelier Index does not appear to be widely applicable to AFBC leachates other than perhaps for a rough approximation. Langelier's original work dealt with water-distribution systems that used concrete pipe. Corrosion and scaling were related to materials used in the systems and chemistries associated with drinking waters which were more neutral than the AFBC leachates. The applicability of extending this index to the limits required for the laboratory-scale leachates is, at best, questionable.

4.2.3 Aeration Experiments. During the aeration reaction or recarbonation, carbon dioxide reacts with calcium hydroxide to form calcium carbonate:

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

The CO_2 requirements to convert calcium hydroxide to calcium carbonate can be calculated by the following (15):

$$CO_2 \text{ in mg/L} = \frac{\text{molecular weight of } CO_2}{\text{molecular weight of } CaCO_3} \times OH^- \text{ alkalinity in mg/L as } CaCO_3$$

$$= 0.44 \times (OH^- \text{ alkalinity in mg/L as } CaCO_3)$$

Two applications for recarbonation exist. In single-stage recarbonation, the pH is reduced from 11 or 12 to 7, or any desired value, in one basin. Little calcium is precipitated with this system. In two-stage recarbonation two basins are used, separated by an intermediate settling tank. In the first stage, the pH is reduced from 11 or 12 to 9.3, the pH at which the solubility of calcium carbonate is lowest. This results in the formation of calcium carbonate and a rapidly settling floc. In the intermediate basin, the reaction goes to completion and the precipitate settles out. The effluent from the intermediate basin is then treated in the second stage to reduce the pH to the desired value (21).

The two-stage recarbonation process results in an effluent with a slight increase in hardness and produces pure calcium carbonate as a waste product, which could be recovered as sorbent for the AFBC combustor. The effluent calcium concentrations can be as low as 40 mg/L (21).

The efficiency of CO_2 utilization in the aeration experiments can be calculated. For the tests conducted at a "G" value of 2080 s^{-1}, 0.83 m^3/L of air was required to achieve the desired pH. Based on an atmospheric CO_2 concentration of 0.034 %, the CO_2 dosage supplied was 872 mg/L. The theoretical requirement was calculated to be 489 mg/L. The efficiency of CO_2 use, therefore, was about 56 %. In contrast, at a "G" value of 430 s^{-1}, 1.25 m^3/L of air was required to achieve the desired pH. For this case, the efficiency of CO_2 use was 33 %. It may be possible to further improve the efficiency of the gas/liquid reaction by optimizing the gas bubble size produced by the diffuser.

Figure 7 shows the effect of mixing on the volume of air required to achieve the desired pH. The relationship has a regression coefficient of -0.99 showing an almost perfect inverse relationship between the two variables. A "G" value of 2080 s^{-1} represents the maximum reasonably achievable in wastewater treatment plants. Further improvement in the reaction efficiency cannot come from improved mixing but rather better gas transfer as previously mentioned, or by using a gas source richer in CO_2.

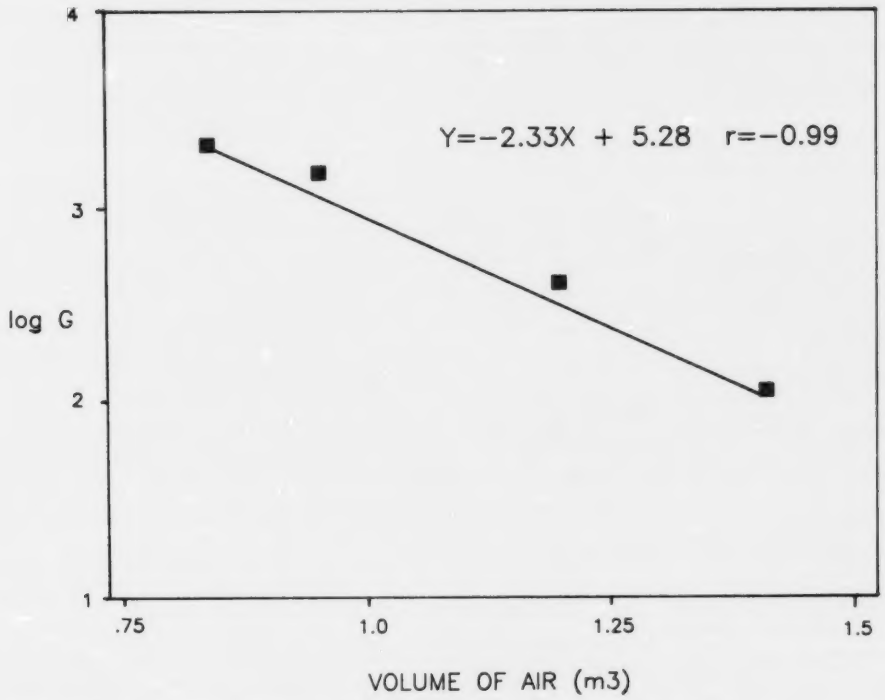

FIGURE 7 EFFECT OF MIXING ON REQUIRED AIR

One possible source of CO_2 in an AFBC unit would be the stack gases which would contain high concentrations from the combustion of the coal and the calcining of limestone in the bed. Keeping all other parameters constant, any increase in CO_2 would reduce the gas volume requirements directly. That is, doubling the CO_2 gas concentration would half the required gas volume, and as a result, half the reaction time. Theoretically, the use of pure CO_2 would reduce the reaction time almost thirty-fold to essentially an instantaneous reaction which could be completed in a small rapidly-mixed basin.

In terms of the design of a leachate treatment process, a trade off would exist. Improved reaction rates would be possible by using higher mixing intensities. This, however, requires greater mixing horsepower although, a smaller reaction vessel could be used. The costs of alkaline AFBC leachate treatment at the pilot scale for a variety of treatment methods have been compared in a previous study (22). At a "G" value of about 100 s^{-1}, the cost of aeration was in the range of \$ 0.37/m^3 (1985). In comparison, the cost of treatment with H_2SO_4 was \$ 0.73/m^3 (1985). These costs were for materials only and did not include capital, construction, labour or maintenance costs. Assuming the improved efficiencies of the aeration reactions at greater mixing intensities found in this study, the cost of aeration using a "G" value of 2080 s^{-1} would be in the range of

$ 0.23/m^3 (1985). This would be the most cost effective of the options investigated, based on this very limited cost evaluation.

In certain leachate-handling systems, contact with the atmosphere might be preferred due to the neutralizing effect of adsorbed CO_2 gases from the atmosphere. The advantage of such a system would be reduced leachate treatment costs. For example, large shallow lagoons could be used to permit contact between the atmosphere and wastewater. This reaction would accomplish the same goal; however, it would require a much larger reaction time and would be subject to other economic, climatic and technical drawbacks of lagoon-based treatment designs.

4.2.4 PHREEQE Predictions. The chemical characteristics of untreated and treated laboratory-scale produced leachates with the leachates simulated using the chemical equilibirum model PHREEQE for a representative AFBC residue (Test Run 1, bed material) are compared in Table 10. In general, the model was able to predict actual leachates well.

Using the limited input data and based on the assumptions mentioned in Section 3, the computer model simulated the laboratory-produced and treated and untreated leachates surprisingly well.

TABLE 10 COMPARISON OF LABORATORY-PRODUCED AND COMPUTER-SIMULATED LEACHATES

	Laboratory Produced		Computer Simulated	
Parameter	Untreated	Treated	Closed System	Open System
pH	12.5	7.7	12.66	7.67
TDS	4550	1880	4103	1966
Aluminum	0.05	0.01	95.9	0
Calcium	1340	368	2239	816.4
Iron	0.09	0.04	0	0
Potassium	289	216	139	0
Phosphate	< 1	< 1	0	0
Sulphate	1540	1240	988	1129

Note: All concentrations expressed in mg/L except pH.

The pH, TDS, iron and phosphate parameters were simulated very well using the computerized technique. The effects of the contact of the leachates with CO_2 (aerated in the laboratory and open system for the simulation) showed similar trends for calcium and potassium. The simulation predicted higher concentrations of aluminum and calcium but lower concentrations of sulphate. The higher aluminum concentration in simulated leachate probably occurs because the interaction between calcium, aluminum and silica at the high pH is not considered. For the case of sulphate, the computer was not able to simulate the decrease in concentration which was observed in the laboratory testing. This is not readily explained.

Some deviation between the simulated and laboratory-scale produced leachates was apparent but with further refining of the assumptions concerning the mineral phase, closer agreement will be possible. In any case, the simulated leachates are sufficiently similar chemically that the same conclusions would be reached based on them as those based on the laboratory-scale produced leachates.

A significant benefit of the computer simulations is the ability to estimate the amount of material undissolved under the specified leaching conditions. This was shown in Table 7. For example, $CaSO_4$ remained primarily in the solid phase because the solution was saturated with respect to $CaSO_4 \cdot 2H_2O$. Likewise, all $CaCO_3$ was undissolved in the closed systems. In contrast, the CaS was totally dissolved in all cases, while in the open system greater amounts of $CaCO_3$ were solubilized due to the reaction with CO_2. This type of data is not readily derived from a single cycle of laboratory leach testing.

4.3 Leachate Toxicity and Genotoxicity Characterization

The principal leachate constituents and leachate toxicity of six pairs of untreated and treated leachates are compared in Table 11. The chemical parameters pH, alkalinity, hardness, TDS, calcium, and sulphate were selected because their concentrations were reduced as a result of aeration. All other chemical parameters were either not detected or were not significantly changed as a result of treatment. Also shown are the changes in toxicity of the leachates as determined using the Microtox™, *Selenastrum capricornutum* and *Daphnia magna* procedures. The SOS Chromotest™ genotoxicity assay results are not shown since none of the leachates were found to be genotoxic.

It is difficult to determine individually, the relationship between the chemical constituents of the leachate and the observed toxic response for two reasons. First, the chemistry of the leachates appears to be controlled by their pH. As the pH is reduced

TABLE 11 PRINCIPAL LEACHATE CONSTITUENTS AND LEACHATE TOXICITY OF UNTREATED AND TREATED LEACHATES

Parameter	BED MATERIAL				CYCLONE MATERIAL				BAGHOUSE MATERIAL			
	Run No. 5		Run No. 8		Run No. 5		Run No. 8		Run No. 5		Run No. 8	
	Untreated	Treated	Untreated	Treated	Untreated	Treated	Untreated	Treated	Untreated	Treated	Untreated	Treated
pH (units)	12.3	7.8	12.3	7.8	12.3	7.8	12.3	7.8	8.6	7.6	12.2	7.7
Alkalinity	2200	38	2200	40	2120	36	2180	38	40	24	1720	38
Hardness	3980	1570	3830	1310	3850	1700	4325	1400	3850	3510	3450	2510
TDS	4670	2240	4450	1930	4750	2540	4530	2080	6500	5220	6830	3530
Calcium	1590	627	1530	523	1540	679	1730	559	1540	1410	1380	1000
Sulphate	1690	1490	1570	1270	1700	1550	1600	1330	1100	1280	1560	1170
Microtox™:												
(i) 5-min EC_{50} (% sample volume)	0.66	NT	0.73	NT	0.75	NT	0.94	NT	NT	NT	0.83	NT
(ii) 15-min EC_{50} (% sample volume)	0.63	NT	0.67	NT	0.71	NT	0.88	NT	NT	NT	0.78	NT
Selenastrum capricornutum:												
Growth Inhibition 96-h EC_{50} (% sample volume)	20	NT	20	NT	30	NT	30	NT	30	NT	10	NT
Daphnia magna:												
48-h LC_{50} (% sample volume)	1.8	71	7.8	71	6.4	66	1.8	84	42	71	2.7	62

Note: All results expressed in mg/L except where noted otherwise.
NT means nontoxic

through aeration, the alkalinity and hardness (of which calcium is the main constituent) are reduced through the precipitation of calcium carbonate and, to a lesser extent, calcium sulphate. This would also result in reduced concentrations of sulphate and total dissolved solids. It is difficult, therefore, to isolate the effect of reduced sulphate concentrations, for example, on the toxicity of the leachates as determined using these procedures. Second, only untreated and treated leachates were subjected to toxicity testing in this study. In order to establish the relationship between leachate chemistry and toxicity, it would be necessary to assess the toxicity of a series of partially-treated leachates and relate these results to changes in leachate chemistry.

The data shown in Table 11 indicate a strong trend between decreased pH and reduced toxicity. When the pH of the leachates was neutralized by aeration or by sulphuric acid addition (Table 8), the toxicity was reduced significantly in all three aquatic toxicity tests.

For example, reducing the pH from around 12.3 to less than 7.8 changed the leachate toxicity to Microtox™ bacteria from an EC_{50} of less than 1 % sample volume to nontoxic. In the one case of Run No. 5-baghouse material, the untreated leachate with an original pH of 8.6 was nontoxic. Similarly, reducing the pH over the same range reduced the 96-h EC_{50} for *Selenastrum capricornutum* from between 10 to 30 % to nontoxic. The same trend was evident with the *Daphnia magna* toxicity test results (i.e., 1.8 to 7.8% LC_{50}'s down to 62% to 84% LC_{50}'s when treated).

At the end of Table 8 the dilution of the sample required to lower the pH of the leachates to a range favourable to Microtox™ bacteria (pH 6 to 7) and *Selenastrum capricornutum* (pH 9 to 10) is shown.

It can be noted that the dilution of sample required to achieve such pH ranges is in the same order of magnitude as the EC_{50}'s for test organisms.

Since an EC_{50} denotes the midpoint between 100% toxic effect and no toxic effect, this coincidence further substantiates the contribution of pH to the toxicity of the samples.

Further examination of the data summarized in Table 8 also demonstrates the importance of using a battery of toxicity tests. For example, a wide range in sensitivities of the test species was exhibited to many of the sample leachates. The Microtox™ test was the most sensitive of the three aquatic toxicity tests for untreated leachate samples, while the *Daphnia* test was the most sensitive of the three tests for treated leachate samples.

5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Based on the chemical characterization program and a review of the data, the following conclusions are made:

- The physical characterization of the samples indicates that the physical properties of the residues are not dependent on the fuel and sorbents used. Each of the three residue types were similar for each fuel and sorbent combination. The residues would be troublesome to manage at a disposal site due to their fine particle size and dryness and would not be amenable to disposal by landfilling without conditioning.
- The chemical characteristics of the residues are directly related to the combustion process. The wastes contained trace elements derived from the fuels and sorbents used and were generally similar. Exceptions to this were the increased concentrations of certain elements such as nickel, molybdenum and vanadium in the residue from the combustion of petroleum coke. The main crystalline components were, as expected, $CaSO_4$ and CaO. The CaO was responsible for exothermic reactions for the coal fuel derived wastes but not wastes produced by burning coke. This is probably due to the higher combustion temperatures which affected the residue particle's physical properties. The hydration of the $CaSO_4$ and CaO component of the residue would require large amounts of water. This requirement would likely need to be satisfied before any effect of water addition on the compactability or dust suppression of the waste would be possible.
- Low concentrations of CaS were quantified in the AFBC residues, always less than three percent. CaS may be an artifact of pilot-scale combustion, and there is evidence that it would be present in even lower concentrations in residues from full-scale combustors. The utilization of the residues, particularly for acid neutralization, may be limited as a result of even low concentrations of CaS.
- Results of the leachate testing indicate that uncompacted AFBC residues would produce very alkaline, high TDS leachates. The main dissolved species would be calcium, sulphate and alkalinity. The laboratory-scale testing can produce a worst-case situation and does not consider the reduction of leachate production due to waste changes such as loss of permeability due to strength development following disposal.
- The Langelier Index was judged to be of limited application as a predictive tool for the identification of scaling conditions since the leachate chemistries were significantly different from the waters for which the index was developed. Other more sophisticated techniques are available.
- Aeration of the laboratory-produced leachates indicated that recarbonation of the wastewaters is a possible means to reduce their pH and alkalinity. These tests also predicted that the pH and alkalinity of the wastewaters would decrease following extended contact with the atmosphere such as might be encountered in a lagoon system.
- The effect of mixing regimes on the aeration requirements was demonstrated to be inversely related over a range of "G" values from 100 to 2000 s^{-1}.

- Further improvement in the recarbonation reaction could be made by better control over the gas bubble size which would improve gas/liquid transfer. Only about half of the CO_2 supplied to the wastewater was consumed in the reaction.
- The usefulness of computerized chemical-equilibrium models was demonstrated through the use of PHREEQE. Based on limited waste characterization data and prior assumptions, the model was able to simulate both open and closed systems. The predicted wastewater pH and TDS concentrations were very similar to those produced in the laboratory.
- All untreated alkaline samples produced toxic responses in Microtox™, algal and *Daphnia magna* tests.
- Neutralization of alkaline leachates by aeration or sulphuric acid addition was accompanied by a large reduction in toxic response. Toxicity in neutralized samples was not observed in any Microtox™ or algal assays. *Daphnia magna* testing detected a slight toxic effect in neutralized samples.
- Genotoxicity was not detectable by the SOS Chromotest™ assay in either treated or untreated samples.
- The use of a battery of biological tests in contrast to a single procedure applied, for example, at the start of a tiered protocol, provides a more comprehensive evaluation of leachate toxicity. An additional benefit of the battery approach which was also demonstrated is the wide range in the sensitivities exhibited by the test species to many of the sample leachates.

5.2 Recommendations

Based on this investigation, the following recommendations are made for further study:

- The laboratory-scale leaching protocol used in this study involves conditions unlikely to exist in a landfill disposal site and thus produces leachates which may not be representative of field conditions. Further work should be to develop leaching protocols which better simulate field conditions, possibly by accounting for changes which take place in the wastes during landfilling.
- A major limitation in the development of disposal technologies for AFBC wastes is a lack of thorough understanding of the relationship between the geotechnical properties of the waste and the volume and rate of leachate production. Residues should be further tested to identify optimum disposal regimes in consideration of the residue's geotechnical properties. This would require initial laboratory testing followed by field verification at an operating disposal site.
- The computer model PHREEQE has been demonstrated, at a preliminary level, to simulate laboratory leaching experiences. Further development and refinement of the required input data and mineral phase assumptions are needed to fully demonstrate and exploit the usefulness of this approach.
- In some waste types, particularly the baghouse material leachates, high total organic carbon (TOC) concentrations were found. Futher work is needed to identify the constituents of the TOC and to understand the mechanism of formation.

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APPENDIX A
LABORATORY TEST RESULTS

LIST OF TABLES

Table		Page
A-1	Bed Material Chemical Composition	58
A-2	Cyclone Material Chemical Composition	59
A-3	Baghouse Material Chemical Composition	60
A-4	Bed Material Leachate Characteristics	61
A-5	Cyclone Material Leachate Characteristics	62
A-6	Baghouse Material Leachate	63
A-7	Comparison of Untreated and Treated Bed Material Leachate Characteristics	64
A-8	Comparison of Untreated and Treated Cyclone Material Leachate Characteristics	65
A-9	Comparison of Untreated and Treated Baghouse Material Leachate Characteristics	66
A-10	Comparison of Baghouse Material Leachates Treated at Different Mixing Intensities	67
A-11	Replicate Analyses of Combustion Residues	68
A-12	Replicate Analyses of Bed Material Leachates	69
A-13	Residue Heat Releases	70
A-14	Summary of Specific Gravity Minimum Density and Water Content Determinations	71
A-15	Aeration Test Conditions	72
A-16	Crystalline Composition of AFBC Residues	73

TABLE A-1 BED MATERIAL CHEMICAL COMPOSITION

PARAMETER	COMBUSTION RESIDUE							
	1	2	3	4	5	6	7	8
Aluminum	19600	14500	21000	27000	68800	13500	8340	85600
Arsenic	5	171	17	161	117	249	35	50
Barium	140	122	73.3	83.9	297	108	65.6	464
Beryllium	0.42	0.52	0.94	0.64	2.19	101	0.20	2.76
Calcium	364000	351000	283000	317000	208000	339000	358000	178000
Chromium	45	28	60	18	55	23	23	80
Cobalt	<5	<5	<5	<5	<5	<5	<5	8
Copper	9.7	12.7	14.4	13.3	24.7	25.9	14.6	75.2
Iron	11700	19100	15400	18600	34100	21300	16700	23500
Lead	<5	15	<5	100	355	15	10	50
Magnesium	6680	5730	6030	7150	4630	4160	4210	7770
Manganese	345	2100	103	2050	599	674	541	1560
Molybdenum	70	<20	<20	<20	<20	<20	<20	<20
Nickel	260	26	26	27	32	23	22	47
Silver	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Sodium	900	1000	1000	1700	3700	500	1100	7200
Strontium	394	281	264	310	419	202	186	227
Thorium	<5	<5	<5	<5	<5	<5	<5	11
Titanium	1510	726	1260	1190	2750	782	504	2990
Vanadium	613	20.8	34.8	28.8	63.0	19.3	33.6	86.9
Zinc	73	219	230	465	104	60	227	275
Zirconium	53	14	25	18	45	18	14	46

*NOTE: All analyses expressed as mg/kg

TABLE A-2 CYCLONE MATERIAL CHEMICAL COMPOSITION

PARAMETER	COMBUSTION RESIDUE							
	1	2	3	4	5	6	7	8
Aluminum	32500	22700	15800	26200	22000	11700	7830	27000
Arsenic	8	96	16	100	78	122	19	42
Barium	232	79.8	100	79.7	129	96.8	135	362
Beryllium	<0.05	2.02	1.59	1.15	1.20	1.74	0.17	1.42
Calcium	331000	207000	268000	220000	230000	234000	319000	125000
Chromium	63	75	40	55	48	30	20	40
Cobalt	20	17	9	<5	<5	<5	<5	<5
Copper	24.9	43.6	15.1	31.8	26.0	34.2	23.5	58.1
Iron	17300	69600	34800	70800	52600	69800	41300	34900
Lead	10	105	5	100	85	30	50	35
Magnesium	7060	6450	3870	10400	2850	1780	2170	4400
Manganese	529	1630	108	1950	728	522	639	1250
Molybdenum	110	<20	<20	<20	<20	<20	<20	<20
Nickel	1060	50	30	39	35	23	19	28
Silver	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Sodium	2100	1100	600	1500	900	200	1300	1400
Strontium	404	191	223	194	186	142	146	133
Thorium	<5	<5	<5	<5	<5	<5	<5	<5
Titanium	3340	938	801	950	836	736	358	1020
Vanadium	2720	39.9	68.8	38.1	38.4	20.7	29.6	42.4
Zinc	67	300	273	555	93	56	484	178
Zirconium	121	18	23	17	16	15	10	15

*NOTE: All analyses expressed as mg/kg

TABLE A-3 BAGHOUSE MATERIAL CHEMICAL COMPOSITION

PARAMETER	COMBUSTION RESIDUE						
	1	2	3	4	5	6	8
Aluminum	44700	49000	53300	69900	54800	47300	41100
Arsenic	11	331	50	343	360	360	176
Barium	190	68.8	165	110	229	105	170
Beryllium	<0.05	8.42	7.06	8.92	7.31	9.71	4.53
Calcium	292000	133000	118000	92100	98900	105000	160000
Chromium	145	110	120	145	100	90	65
Cobalt	23	27	19	42	39	29	17
Copper	66.6	110	58.4	115	94.5	117	81.3
Iron	22300	110000	92800	143000	172000	218000	53700
Lead	10	195	105	100	980	390	245
Magnesium	7940	4370	5250	10100	4670	2190	8400
Manganese	642	1550	339	1720	1260	620	1620
Molybdenum	190	<20	<20	<20	<20	<20	<20
Nickel	1970	180	363	152	91	80	59
Silver	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Sodium	4100	4300	4100	7400	4100	2800	4600
Strontium	434	278	233	334	324	279	294
Thorium	17	27	<5	<5	<5	<5	<5
Titanium	4710	2750	3660	3480	2590	2960	1920
Vanadium	4320	279	904	246	144	138	84.2
Zinc	93	806	577	1110	307	403	590
Zirconium	155	54	100	66	46	52	33

*NOTE: All analyses expressed as mg/kg

TABLE A-4 BED MATERIAL LEACHATE CHARACTERISTICS

PARAMETER	DETECTION LIMIT	COMBUSTION RESIDUE							
		1	2	3	4	5	6	7	8
pH (units)	0.05	12.5	12.2	12.3	12.2	12.3	12.3	12.2	12.3
Alkalinity	<1	2280	2080	2200	2200	2200	2320	2120	2200
Hardness	<1	3350	3430	3300	3800	3980	3480	3980	3830
T.D.S.	<2	4550	4510	4790	4640	4670	4700	4670	4450
Conductivity (uS/cm)	-	6000	5800	5900	5900	5900	6000	5900	5900
Aluminum	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Arsenic	<0.001	<0.001	0.001	<0.001	<0.001	0.004	0.008	0.001	0.002
Barium	<0.005	0.183	0.375	2.76	0.096	0.122	0.193	0.070	0.096
Beryllium	<0.0005	<0.0005	0.0010	0.0016	<0.0005	0.0011	0.0021	<0.0005	<0.0005
Boron	<0.004	0.031	0.040	0.047	0.038	0.036	0.519	0.231	0.534
Cadmium	<0.01	0.04	0.05	0.05	0.05	0.05	0.06	0.04	0.05
Calcium	<0.01	1340	1370	1320	1520	1590	1390	1590	1530
Chloride	<0.1	3.30	5.70	3.10	6.80	8.50	1.50	15.5	3.70
Chromium	<0.01	0.04	0.04	0.08	0.02	0.03	0.06	0.03	0.03
Cobalt	<0.05	<0.05	<0.05	<0.05	<0.05	0.07	<0.05	<0.05	<0.05
Copper	<0.009	0.021	0.016	0.012	0.015	0.017	<0.009	0.013	0.012
Fluoride	<0.5	1.8	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.9
Iron	<0.01	0.09	0.09	0.07	0.09	0.10	0.10	0.10	0.11
Lead	<0.05	<0.05	<0.05	0.35	<0.05	0.10	<0.05	<0.05	<0.05
Magnesium	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	114	<0.01	<0.01
Manganese	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	9.35	<0.01	<0.01
Molybdenum	<0.2	1.2	2.4	5.2	0.3	0.4	0.6	0.3	0.3
Nickel	<0.05	0.09	0.08	0.09	0.08	0.09	0.12	0.09	0.09
Phosphate (PO_4)	<1	<1	<1	<1	<1	<1	<1	<1	<1
Potassium	<1	289	201	479	<1	4	63	2	4
Silica	<0.05	0.24	0.26	0.34	0.15	0.25	0.91	0.19	0.19
Silver	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Sodium	<1	28	21	50	<1	2	32	1	<1
Strontium	<0.05	3.52	3.86	3.31	3.07	2.65	2.49	2.31	4.28
Sulphate	<0.05	1540	1600	1720	1650	1690	1710	1140	1570
Thorium	<0.05	0.09	0.12	0.09	0.11	0.13	0.08	0.10	0.06
Titanium	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Toc	<0.5	19.5	28.0	4.0	7.5	30.0	5.5	1.5	4
Vanadium	<0.005	0.025	0.032	0.224	0.024	0.019	0.014	0.020	0.015
Zinc	<0.05	0.06	0.06	<0.05	0.07	0.06	<0.05	0.06	0.07
Zirconium	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05

*NOTE: All analyses expressed as mg/L except where noted

TABLE A-5

CYCLONE MATERIAL LEACHATE CHARACTERISTICS

PARAMETER	DETECTION LIMIT	COMBUSTION RESIDUE							
		1	2	3	4	5	6	7	8
pH (units)	0.05	12.5	12.2	12.3	12.3	12.3	12.2	12.3	12.3
Alkalinity	<1	2600	2160	2140	2260	2120	2160	2120	2180
Hardness	<1	3925	3850	3050	3700	3850	3750	3800	4325
T.D.S.	<2	4300	5010	4790	4770	4750	4790	4920	4530
Conductivity (uS/cm)	-	6300	5900	5800	5900	5900	5900	5900	5900
Aluminum	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Arsenic	<0.001	<0.001	0.001	0.001	0.002	0.002	0.003	<0.001	0.002
Barium	<0.005	0.147	0.147	0.762	0.162	0.190	0.154	0.189	0.776
Beryllium	<0.0005	0.0011	0.0006	<0.0005	0.0007	0.0015	0.0015	0.0014	0.0013
Boron	<0.004	0.041	0.034	0.051	0.071	0.097	0.040	0.047	0.099
Cadmium	<0.01	0.04	0.04	0.03	0.03	0.03	0.04	0.03	0.04
Calcium	<0.01	1570	1540	1220	1480	1540	1500	1520	1730
Chloride	<0.1	1.80	108	6.50	44.8	43.1	8.00	76.9	27.8
Chromium	<0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.06
Cobalt	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.06	<0.05	<0.05
Copper	<0.009	0.013	0.009	<0.009	0.014	0.014	0.022	0.012	0.013
Fluoride	<0.5	2.4	<0.5	1.3	<0.5	<0.5	<0.5	<0.5	<0.5
Iron	<0.01	0.09	0.08	0.06	0.08	0.09	0.11	0.08	0.10
Lead	<0.05	<0.05	<0.05	0.05	<0.05	<0.05	<0.05	<0.05	0.15
Magnesium	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Manganese	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Molybdenum	<0.2	0.4	0.4	1.0	0.3	0.4	0.3	0.3	0.6
Nickel	<0.05	0.08	0.08	0.07	0.08	0.07	0.08	0.08	0.09
Phosphate (PO_4)	<1	<1	<1	<1	<1	<1	<1	<1	<1
Potassium	<1	<1	<1	30	<1	4	<1	<1	6
Silica	<0.05	0.16	0.16	1.62	0.14	0.16	0.15	0.21	0.37
Silver	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Sodium	<1	<1	<1	15	2	7	<1	<1	7
Strontium	<0.05	1.42	2.27	1.84	1.46	2.53	2.01	2.54	2.01
Sulphate	<0.05	1230	1660	1720	1680	1700	1800	1690	1600
Thorium	<0.05	0.15	0.12	0.12	0.16	0.15	0.18	0.13	0.11
Titanium	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Toc	<0.5	33.0	2.0	3.5	33.0	3.0	2.5	40.0	6.5
Vanadium	<0.005	0.015	0.010	0.023	0.013	0.016	0.023	0.013	0.011
Zinc	<0.05	<0.05	<0.05	<0.05	0.06	0.10	0.08	0.06	0.06
Zirconium	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05

*NOTE: All analyses expressed as mg/L except where noted

TABLE A-6 BAGHOUSE MATERIAL LEACHATE CHARACTERISTICS

PARAMETER	DETECTION LIMIT	COMBUSTION RESIDUE						
		1	2	3	4	5	6	8
pH (units)	0.05	12.3	8.1	10.0	11.6	8.6	11.8	12.2
Alkalinity	<1	2040	50	440	440	40	620	1720
Hardness	<1	2270	3730	3850	2600	3850	3730	3450
T.D.S.	<2	5390	7220	3970	4610	6500	5310	6830
Conductivity (uS/cm)	-	5900	4800	2950	3700	4500	4200	5900
Aluminum	<0.05	15.2	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Arsenic	<0.001	0.001	0.009	0.003	0.057	0.154	0.021	0.016
Barium	<0.005	0.030	0.111	0.126	0.573	0.103	0.166	0.246
Beryllium	<0.0005	<0.0005	0.0012	0.0006	<0.0005	0.0006	0.0007	0.0014
Boron	<0.004	4.20	0.058	0.043	0.086	0.044	0.047	0.967
Cadmium	<0.01	0.04	0.05	0.05	0.04	0.04	0.04	0.04
Calcium	<0.01	908	1490	1540	1040	1540	1490	1380
Chloride	<0.1	76.2	1820	193	501	1500	661	893
Chromium	<0.01	0.03	0.02	0.02	0.04	0.02	0.02	0.02
Cobalt	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Copper	<0.009	0.011	0.015	0.012	<0.009	0.012	0.010	<0.009
Fluoride	<0.5	8.6	2.2	8.6	<0.5	<0.5	<0.5	<0.5
Iron	<0.01	0.08	0.10	0.08	0.07	0.08	0.08	0.07
Lead	<0.05	<0.05	<0.05	0.10	0.05	<0.05	0.05	<0.05
Magnesium	<0.01	0.99	<0.01	<0.01	0.05	<0.01	<0.01	4.19
Manganese	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Molybdenum	<0.2	1.2	0.3	0.3	0.9	0.3	0.3	0.6
Nickel	<0.05	<0.05	0.08	0.07	0.07	0.07	0.07	0.07
Phosphate (PO_4)	<1	<1	<1	<1	<1	<1	<1	<1
Potassium	<1	69	<1	3	46	<1	2	6
Silica	<0.05	0.38	0.14	0.27	2.95	0.17	0.21	0.42
Silver	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Sodium	<1	29	<1	3	35	<1	1	5
Strontium	<0.05	1.21	2.39	2.39	2.26	1.40	3.06	1.96
Sulphate	<0.05	1610	1450	1790	1640	1100	1650	1560
Thorium	<0.05	0.09	0.16	0.13	0.12	0.10	0.10	0.14
Titanium	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Toc	<0.5	22.0	42.0	14.0	7.0	14.0	52.0	2.0
Vanadium	<0.005	0.323	0.021	0.018	0.075	0.009	0.007	0.032
Zinc	<0.05	<0.05	0.09	0.07	<0.05	<0.05	<0.05	<0.05
Zirconium	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05

*NOTE: All analyses expressed as mg/L except where noted

TABLE A-7 COMPARISON OF UNTREATED AND TREATED BED MATERIAL LEACHATE CHARACTERISTICS

PARAMETER	COMBUSTION TEST RUN NUMBER					
	NO. 1		NO. 5		NO. 8	
	UNTREATED	TREATED	UNTREATED	TREATED	UNTREATED	TREATED
pH (units)	12.5	7.7	12.3	7.8	12.3	7.8
Alkalinity	2280	42	2200	38	2200	40
Hardness	3350	920	3980	1570	3830	1310
T.D.S.	4550	1880	4670	2240	4450	1930
Conductivity (uS/cm)	6000	1670	5900	1780	5900	1540
Aluminum	<0.05	<0.01	<0.05	<0.01	<0.05	<0.01
Arsenic	<0.001	<0.001	0.004	0.001	0.002	0.001
Barium	0.183	0.038	0.122	0.034	0.096	0.052
Beryllium	<0.0005	<0.0005	0.0011	<0.0005	<0.0005	<0.0005
Boron	0.031	0.024	0.036	0.041	0.534	0.038
Cadmium	0.04	<0.01	0.05	<0.01	0.05	<0.01
Calcium	1340	368	1590	627	1530	523
Chromium	0.04	0.03	0.03	0.02	0.03	<0.01
Cobalt	<0.05	0.03	0.07	0.11	<0.05	<0.05
Copper	0.021	<0.009	0.017	0.017	0.012	0.013
Iron	0.09	0.04	0.10	0.07	0.11	0.04
Lead	<0.05	<0.05	0.10	<0.05	<0.05	<0.05
Magnesium	<0.01	0.05	<0.01	<0.01	<0.01	0.05
Manganese	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Molybdenum	1.2	1.0	0.4	0.4	0.3	<0.2
Nickel	0.09	<0.05	0.09	0.11	0.09	<0.05
Phosphate (PO_4)	<1	<1	<1	<1	<1	<1
Potassium	289	216	4	7	4	4
Silica	0.24	0.27	0.25	0.41	0.19	0.22
Silver	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Sodium	28	22	2	2	1	<1
Strontium	3.52	2.25	2.65	1.05	4.28	1.64
Sulphate	1540	1240	1690	1490	1570	1270
Thorium	0.09	<0.05	0.13	<0.05	0.06	<0.05
Titanium	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Toc	19.5	4.0	30.0	3.0	4.0	8.0
Vanadium	0.025	0.011	0.019	0.025	0.015	0.013
Zinc	0.06	<0.05	0.06	<0.05	0.07	<0.05
Zirconium	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05

*NOTE: All analyses expressed as mg/L except where noted

TABLE A-8 COMPARISON OF UNTREATED AND TREATED CYCLONE MATERIAL

LEACHATE CHARACTERISTICS

PARAMETER	COMBUSTION TEST RUN NUMBER					
	NO. 1		NO. 5		NO. 8	
	UNTREATED	TREATED	UNTREATED	TREATED	UNTREATED	TREATED
pH (units)	12.5	7.8	12.3	7.8	12.3	7.8
Alkalinity	2600	42	2120	36	2180	38
Hardness	3925	807	3850	1700	4325	1400
T.D.S.	4300	1600	4750	2540	4530	2080
Conductivity (uS/cm)	6300	1540	5900	2020	5900	1680
Aluminum	<0.05	<0.01	<0.05	<0.01	<0.05	<0.01
Arsenic	<0.001	<0.001	0.002	<0.001	0.002	<0.001
Barium	0.147	0.098	0.190	0.050	0.776	0.066
Beryllium	0.0011	<0.0005	0.0015	<0.0005	0.0013	<0.0005
Boron	0.041	0.029	0.097	0.049	0.099	0.044
Cadmium	0.04	<0.01	0.03	<0.01	0.04	<0.01
Calcium	1570	323	1540	679	1730	559
Chromium	0.02	0.03	0.02	0.03	0.06	0.03
Cobalt	<0.05	0.07	<0.05	0.12	<0.05	0.09
Copper	0.013	<0.009	0.014	0.026	0.013	0.019
Iron	0.09	0.05	0.09	0.09	0.10	0.06
Lead	<0.05	<0.05	<0.05	<0.05	0.15	<0.05
Magnesium	<0.01	0.02	<0.01	0.03	<0.01	<0.01
Manganese	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Molybdenum	0.4	2.0	0.4	0.4	0.6	0.3
Nickel	0.08	<0.05	0.07	0.07	0.09	<0.05
Phosphate (PO_4)	<1	<1	<1	<1	<1	<1
Potassium	<1	176	4	8	6	4
Silica	0.16	0.58	0.16	0.32	0.37	0.29
Silver	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Sodium	<1	20	7	4	7	3
Strontium	1.42	2.65	2.53	2.48	2.01	1.91
Sulphate	1230	970	1700	1550	1600	1330
Thorium	0.15	<0.05	0.15	<0.05	0.11	<0.05
Titanium	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Toc	33.0	2.0	3.0	6.0	6.5	4.0
Vanadium	0.015	0.025	0.016	0.032	0.011	0.028
Zinc	<0.05	<0.05	0.10	<0.05	0.06	<0.05
Zirconium	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05

*NOTE: All analyses expressed as mg/L except where noted

TABLE A-9 COMPARISON OF UNTREATED AND TREATED BAGHOUSE MATERIAL

LEACHATE CHARACTERISTICS

PARAMETER	COMBUSTION TEST RUN NUMBER					
	NO. 1		NO. 5		NO. 8	
	UNTREATED	TREATED	UNTREATED	TREATED	UNTREATED	TREATED
pH (units)	12.3	7.9	8.6	7.6	12.2	7.7
Alkalinity	2040	60	40	24	1720	38
Hardness	3230	1260	3850	3510	3450	2510
T.D.S.	5390	3030	6500	5220	6830	3530
Conductivity (uS/cm)	5900	2510	4500	3820	5900	2800
Aluminum	15.2	<0.01	<0.05	<0.01	<0.05	<0.01
Arsenic	0.001	<0.001	0.154	0.038	0.016	0.001
Barium	2.93	0.202	0.103	0.131	0.246	0.076
Beryllium	<0.0005	<0.0005	0.0006	<0.0005	0.0014	<0.0005
Boron	0.060	0.045	0.044	0.990	0.967	0.086
Cadmium	0.04	<0.01	0.04	<0.01	0.04	<0.01
Calcium	1290	502	1540	1410	1380	1000
Chromium	0.10	0.10	0.02	0.03	0.02	0.05
Cobalt	<0.05	0.08	<0.05	0.07	<0.05	0.15
Copper	0.011	0.028	0.012	0.013	<0.009	0.022
Iron	0.08	0.06	0.08	0.08	0.07	0.08
Lead	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Magnesium	0.09	0.03	<0.01	6.36	4.19	<0.01
Manganese	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Molybdenum	6.3	4.9	0.3	0.6	0.6	0.6
Nickel	<0.05	<0.05	0.07	0.10	0.07	0.10
Phosphate (PO_4)	<1	<1	<1	<1	<1	<1
Potassium	501	435	<1	7	6	11
Silica	0.38	0.48	0.17	0.51	0.42	0.44
Silver	<0.005	0.040	<0.005	<0.005	<0.005	<0.005
Sodium	53	44	<1	7	5	7
Strontium	3.95	2.43	1.40	2.03	1.96	1.64
Sulphate	1610	1440	1100	1280	1560	1170
Thorium	<0.05	<0.05	0.10	<0.05	0.14	<0.05
Titanium	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Toc	22.0	4.0	14.0	2.5	2.0	7.0
Vanadium	0.323	0.046	0.009	0.042	0.032	0.032
Zinc	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Zirconium	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05

*NOTE: All analyses expressed as mg/L except where noted

TABLE A-10 COMPARISON OF BAGHOUSE MATERIAL LEACHATES TREATED AT DIFFERENT MIXING INTENSITIES

PARAMETER	TEST CONDITIONS				
	UNTREATED	AIR ONLY	MIXING-195 RPM	MIXING-450 RPM	MIXING-560 RPM
pH (units)	12.3	8.4	7.9	8.0	8.3
Alkalinity	2040	58	60	56	58
Hardness	3230	1300	1260	1220	1280
T.D.S.	5390	3080	3030	2880	3010
Conductivity (uS/cm)	5900	2680	2510	2400	2550
Aluminum	15.2	<0.01	<0.01	<0.01	<0.01
Arsenic	0.001	<0.001	<0.001	<0.001	<0.001
Barium	2.93	0.261	0.202	0.215	0.209
Beryllium	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Boron	0.060	0.051	0.045	0.052	0.052
Cadmium	0.04	<0.01	<0.01	<0.01	<0.01
Calcium	1290	519	502	487	512
Chromium	0.10	0.09	0.10	0.09	0.09
Cobalt	<0.05	<0.05	0.08	<0.05	<0.05
Copper	0.011	0.020	0.028	0.053	0.113
Iron	0.08	0.05	0.06	0.04	0.05
Lead	<0.05	<0.05	<0.05	<0.05	<0.05
Magnesium	0.09	0.07	0.03	0.02	<0.01
Manganese	<0.01	<0.01	<0.01	<0.01	<0.01
Molybdenum	6.3	5.7	4.9	5.5	5.4
Nickel	<0.05	<0.05	<0.05	<0.05	<0.05
Phosphate (PO_4)	<1	<1	<1	<1	<1
Potassium	501	465	435	442	445
Silica	0.38	0.50	0.48	0.49	0.50
Silver	<0.005	<0.005	0.040	0.099	0.165
Sodium	53	49	44	48	48
Strontium	3.95	2.45	2.43	2.46	2.36
Sulphate	1610	1510	1440	1410	1470
Thorium	<0.05	<0.05	<0.05	<0.05	<0.05
Titanium	<0.005	<0.005	<0.005	<0.005	<0.005
Toc	22.0	4.0	6.0	6.0	6.0
Vanadium	0.323	0.079	0.046	0.043	0.075
Zinc	<0.05	<0.05	<0.05	<0.05	<0.05
Zirconium	<0.05	<0.05	<0.05	<0.05	<0.05

*NOTE: All analyses expressed as mg/L except where noted

TABLE A-11

REPLICATE ANALYSES OF COMBUSTION RESIDUES

PARAMETER	BED MATERIALS				CYCLONE MATERIAL				BAGHOUSE MATERIAL		NBS STANDARD FLY ASH	
	Combustion Run Number 3		Combustion Run Number 7		Combustion Run Number 3		Combustion Run Number 7		Combustion Run Number 3		Certified	Measured
	First Analysis	Replicate	First Analysis	Replicate	First Analysis	Replicate	First Analysis	Replicate	First Analysis	Replicate	*Value	Analysis
Aluminum	21000	16400	8340	7170	15800	15600	7830	8750	53300	52200	(%) 14.0	14.4
Arsenic	17	16	35	38	16	14	19	20	50	47	*145 ± 15	139
Barium	73.3	71.1	65.6	63.0	100	91.6	135	135	165	171	(%) 0.15	0.14
Beryllium	0.94	0.86	0.20	0.16	1.59	1.11	0.17	0.29	7.06	7.14	12	12
Calcium	283000	287000	358000	360000	268000	281000	319000	302000	118000	117000	*(%) 1.11 ± .01	1.03
Chromium	60	60	23	24	40	38	20	23	120	123	*196 ± 6	185
Cobalt	<5	<5	<5	<5	9	<5	<5	<5	19	22	46	35
Copper	14.4	16.0	14.6	16.6	15.1	16.3	23.5	26.8	58.4	60.5	*118 ± 3	112
Iron	15400	13900	16700	21000	34800	30600	41300	39400	92800	94500	*(%) 9.40 ± 0.10	9.60
Lead	<5	<5	10	<5	5	<5	50	40	105	150	*72.4 ± 0.4	60
Magnesium	6030	5670	4210	4060	3870	3930	2170	2210	5250	5200	*(%) 0.455 ± 0.010	0.458
Manganese	103	109	541	516	108	107	639	606	339	334	190	174
Molybdenum	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	29	<20
Nickel	26	25	22	23	30	27	19	25	363	346	*127 ± 4	129
Silver	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	-	-
Sodium	1000	900	1100	1000	600	600	1300	1400	4100	4100	*(%) 0.17 ± 0.01	0.20
Strontium	264	254	186	197	223	234	146	145	233	233	*830 ± 30	789
Thorium	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	*24.7 ± 0.3	27
Titanium	1260	986	504	467	801	792	358	371	3660	3700	(%) 0.8	0.8
Vanadium	34.8	31.4	33.6	31.6	68.8	66.7	29.6	34.7	904	883	300	296
Zinc	230	285	227	217	273	256	484	521	577	586	*220 ± 10	231
Zirconium	25	21	14	14	23	22	10	11	100	98	-	-

*NOTE: All analyses expressed in mg/kg except where noted

TABLE A-12 REPLICATE ANALYSES OF BED MATERIAL LEACHATES

PARAMETER	METHOD BLANK	COMBUSTION RUN NO. 5	
		INITIAL	REPLICATE
pH (units)	7.4	12.3	12.3
Alkalinity	<1	2200	2200
Hardness	<1	4200	4050
T.D.S.	<2	4670	4650
Conductivity (uS/cm)	-	5900	5900
Aluminum	<0.01	0.55	0.48
Arsenic	<0.001	0.002	0.002
Barium	<0.005	0.111	0.110
Beryllium	<0.0005	0.0006	0.0007
Boron	<0.004	0.057	0.060
Cadmium	<0.01	<0.01	<0.01
Calcium	0.15	1680	1620
Chromium	<0.01	0.02	0.02
Cobalt	<0.05	<0.05	<0.05
Copper	<0.009	0.010	0.009
Iron	<0.01	0.08	0.08
Lead	<0.05	<0.05	<0.05
Magnesium	0.03	<0.01	<0.01
Manganese	<0.01	<0.01	<0.01
Molybdenum	<0.2	0.3	0.3
Nickel	<0.05	0.07	0.08
Phosphate (PO_4)	<1	<1	<1
Potassium	<1	<1	<1
Silica	<0.05	0.16	0.17
Silver	<0.005	<0.005	<0.005
Sodium	<1	<1	<1
Strontium	0.003	1.44	1.44
Sulphate	<0.05	1670	1660
Thorium	<0.05	<0.05	<0.05
Titanium	<0.005	<0.005	<0.005
Toc	<0.5	30	29
Vanadium	<0.005	0.007	0.013
Zinc	<0.05	<0.05	<0.05
Zirconium	<0.05	<0.05	<0.05

NOTE: All analyses expressed in mg/L except where noted

TABLE A-13 RESIDUE HEAT RELEASES

Sample	Waste Type	ΔT (°C)	-ΔH (KJ/kg)
1	bed	2	46.8
	cyclone	1.5	35.1
	baghouse	0	0
2	bed	11	257.6
	cyclone	9.5	222.5
	baghouse	0	0
3	bed	5.5	128.8
	cyclone	6	140.5
	baghouse	0.5	11.7
4	bed	10	234.2
	cyclone	10	234.2
	baghouse	11	257.6
5	bed	4	93.7
	cyclone	13.5	316.1
	baghouse	0.5	11.7
6	bed	5.5	128.8
	cyclone	11	257.6
	baghouse	0.5	11.7
7	bed	10.5	245.9
	cyclone	19	444.9
	baghouse	-	
8	bed	3	70.3
	cyclone	6	140.5
	baghouse	0.5	11.7

NOTE: All temperature rise data based on a liquid to solid ratio of 5:1 except for sample 3 baghouse material which was tested at 10:1 due to limited amount of sample available.

TABLE A-14

SUMMARY OF SPECIFIC GRAVITY
MINIMUM DENSITY AND WATER CONTENT DETERMINATIONS

Sample No.	Specific Gravity[1]	Minimum Density[3] (Mg/m^3)	Wt. of Sample Before Heating (g)	Wt. of Sample After Heating (g)	Water Content (%)	Remarks
S-B-1	2.82	1.419	352.0	352.0	0	
S-B-2	2.81	1.548	495.6	497.4	Note 4	Swelling
S-B-4	2.79	1.615	501.1	502.8	Note 4	Swelling
S-B-5	2.73	1.587	538.5	541.1	Note 4	Swelling
S-B-6	2.77	1.303	253.3	254.2	Note 4	Swelling
S-B-7	2.73	1.250	162.3	162.8	Note 4	Swelling
S-B-8	2.58	1.545	523.3	526.1	Note 4	Swelling
S-BH-1	2.83	0.951	217.2	216.6	0.3	
S-BH-2	2.59	0.257	165.3	131.2	26.0	
S-BH-4	2.76	0.709	139.7	138.6	0.8	
S-BH-5	2.69	0.699	105.7	99.4	6.3	
S-BH-6	2.92	0.381	169.8	167.4	1.4	
S-BH-8	2.44	0.671	118.2	115.2	2.6	
S-C-1	2.77	1.322	298.3	298.5	Note 4	Swelling
S-C-2	2.61	0.562	297.1	295.1	0.7	
S-C-4	2.55	0.995	227.4	229.1	Note 4	Swelling
S-C-5	2.35	0.484	109.3	109.9	Note 4	Swelling
S-C-6	2.55	1.198	354.8	356.5	Note 4	Swelling
S-C-7	2.62	1.235	159.6	160.4	Note 4	Swelling
S-C-8	2.08	0.849	174.1	175.4	Note 4	Swelling
S-B-5	2.80[2]					

NOTES

1. Specific gravity tests carried out on oven dried samples (except for sample S-B-5, see Note 2).

2. Specific gravity tests carried out on samples as received.

3. Minimum density tests carried out on samples as received.

4. Water content tests carried out by drying at 105°C for 24 hours.

   Swelling indicates that samples gained weight while drying at 105°C (e.g., weight of sample immediately after removal from oven was greater than weight of sample before placing in oven) and continued to swell for several days thereafter.

TABLE A-15

AERATION TEST CONDITIONS

Sample	Test Duration (hr:min)	Mixing (rpm)	Mixing (G, Sec^{-1})	pH Initial (units)	pH Final (units)	Time to Midpoint (hr:min)	Final Volume (mL)	Settling Rate	Supernatant	Sludge Volume (%)
1	39:30	195	430	12.45	8.0	13:50	670	rapid	clear	0.2
2	24:00	195	430	12.55	8.1	13:40	830	slow	cloudy	0.2
3	22:50	195	430	12.35	8.5	10:30	810	med	clear	0.5
4	20:30	195	430	12.45	8.0	12:00	830	rapid	clear	0.2
5	19:00	195	430	12.4	8.05	13:10	910	med	clear	0.2
6	3:15	195	430	8.3	7.75	0:10	990	-	clear	nil
7	19:40	195	430	12.55	8.1	13:00	700	slow	clear	0.2
8	21:05	195	430	12.55	8.05	12:25	790	slow	clear	0.2
9	21:30	195	430	12.3	7.95	10:10	790	slow	clear	0.2
3	22:45	450	1500	12.35	8.15	7:50	750	slow	clear	0.2
3	19:45	0	110	12.4	8.15	11:40	940	-	clear	0.1
3	24:00	560	2080	12.45	8.3	7:20	880	slow	clear	0.5

Note: Test Conditions air flow $0.113 m^3/m$
temperature 20°C

for mechanical mixing $G = \sigma n^3 D^5 / V^{\frac{1}{2}}$;
$\sigma = 2.1$

for aeration only $G = \frac{PV}{u}^{\frac{1}{2}}$

$P = 82\ Qa \log \frac{H+34}{34}$

TABLE A-16 CRYSTALLINE COMPOSITION OF AFBC RESIDUES

Sample	$CaSO_4$	CaS	$CaCO_3$	$Ca_3(PO_4)_2$	CaO (free)	Fe_2O_3	Other, mainly SiO_2 and silicates	LOI_{corr}	Sum
S-B-1	33.61	0.71	1.33	0.15	39.54	1.80	20.06	0.42	97.6
S-B-2	30.17	1.68	8.50	0.13	37.03	3.08	17.15	-1.57	96.3
S-B-3	35.06	0.66	8.76	0.33	26.48	2.50	24.14	0.48	98.4
S-B-4	29.28	nil	5.50	0.13	29.84	3.44	31.95	-2.11	98.0
S-B-5	33.80	1.46	11.08	0.22	22.19	3.90	25.81	-2.57	95.9
S-B-6	39.93	2.92	0.78	1.01	30.40	3.72	11.82	-0.22	90.4
S-B-7	42.94	2.00	0.00	0.15	37.03	3.04	9.2	2.33	96.7
S-B-8	11.17	1.78	3.05	0.15	22.19	3.82	52.92	1.80	96.9
S-C-1	13.05	1.25	0.10	0.22	44.32	2.92	28.73	8.07	98.7
S-C-2	16.59	0.54	8.28	0.13	24.68	12.40	16.75	20.04	99.4
S-C-3	16.37	0.19	17.48	0.28	26.27	6.36	17.01	16.07	100.0
S-C-4	12.60	1.76	8.78	0.15	24.80	12.00	23.11	14.15	97.4
S-C-5	14.45	0.11	8.83	0.15	33.03	8.10	17.17	18.09	99.9
S-C-6	14.11	1.73	19.55	0.74	25.70	10.70	13.18	12.52	98.2
S-C-7	19.23	1.53	6.65	0.15	45.39	8.10	10.50	8.24	99.9
S-C-8	7.26	0.36	3.15	0.17	17.26	7.08	22.94	44.23	101.5
S-BH-1	23.15	2.42	2.44	0.26	28.32	3.30	34.12	0.86	94.9
S-BH-2	24.00	3.01	2.12	0.24	6.21	15.90	27.78	27.90	107.2
S-BH-3	24.36	2.14	3.09	0.76	2.83	13.50	37.38	26.96	111.0
S-BH-4	13.89	0.49	3.51	0.26	4.87	20.50	40.05	22.35	105.9
S-BH-5	16.35	0.56	6.77	0.42	3.37	23.00	29.29	27.50	107.3
S-BH-6	15.98	0.80	11.60	2.16	0.95	29.60	31.43	13.52	106.0
S-BH-8	14.70	1.24	14.25	0.28	8.22	8.06	25.54	31.56	103.8

APPENDIX B
RESULTS FROM COMPUTER MODELLING

Example of the conversion of reported substance weight percent to moles of substance per litre of distilled water. Sample S-B-1.

Constituent	Wt (%)	Sample S-B-1 (g/L)	Mole/L
$CaSO_4$	33.61	16.805	0.24688
CaS	0.71	0.355	0.004921
$CaCO_3$	1.33	0.665	0.006644
$Ca_3(PO_4)_2$	0.15	0.075	0.000242
CaO	39.54	19.77	0.35253
Fe_2O_3	1.80	0.90	0.005636
SiO_2	20.06	10.03	0.16693

Example of the calculation of total moles of each element for input to PHREEQE program.

	Sample S-B-1								
	Concentration								
Constituent	Ca^{2+}	SO_4^{2-}	S^{2-}	O_2	CO_3	PO_4^{3-}	e^-	Fe^{3+}	SiO_2
$CaSO_4$	0.24688	0.24688							
CaS	0.000492		0.000492	0.009842					
$CaCO_3$	0.006644				0.006644				
$Ca_3(PO_4)_2$	0.0007254					0.0002436			
$Ca(OH)_2$	0.35253								
Fe_2O_3							0.016908	0.005636	
SiO_2									0.16693
Total	0.6117004	0.24688	0.000492	0.009842	0.006644	0.0002436	0.016908	0.005636	0.16693

Example of PHREEQE program listings for closed (CO_2) system and open (CO_2) system simulations. Sample S-B-1.

```
AFBC SAMPLE S-B-1.  CLOSED SYSTEM. NO CO2 CONTACT
0040011000 1 8        0.0
SOLUTION 1
DIST. WATER WITH 8 COMPONENT REACTION, NO MINERAL CONSTRAINTS. S-B-1
  0  0 2      6.20       7.00        20.0        1.00
STEPS
  1.00
REACTION
    4   0.612    0.0     16   0.247   6.000   16   0.005  -2.000   32   0.010   4.000
   15   0.007   4.000    19   0.000   0.0      8   0.006   3.000    0   0.017   0.0
```

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SOLUTION NUMBER 1 DIST. WATER WITH 8 COMPONENT REACTION, NO MINERAL CONSTRAINTS. S-8-1

TOTAL MOLALITIES OF ELEMENTS

ELEMENT	MOLALITY	LOG MOLALITY	CONC MG/L

PURE WATER

----DESCRIPTION OF SOLUTION----

PH =	6.2000
PE =	7.0000
ACTIVITY H2O =	1.0000
IONIC STRENGTH =	0.0000
TEMPERATURE =	20.0000
ELECTRICAL BALANCE =	6.2052E-07
THOR =	-5.9295E-30
TOTAL ALKALINITY =	1.0851E-08
ITERATIONS =	5
TDS MG/L =	0.0

DISTRIBUTION OF SPECIES

I	SPECIES	Z	MOLALITY	LOG MOLALITY	ACTIVITY	LOG ACTIVITY	GAMMA	LOG GAMMA
1	H+	1.0	6.31374E-07	-6.1997	6.30957E-07	-6.2000	9.99340E-01	-0.0003
2	E-	-1.0	1.00000E-07	-7.0000	1.00000E-07	-7.0000	1.00000E+00	0.0
3	H2O	0.0	1.00000E+00	-0.0000	1.00000E+00	-0.0000	1.00000E+00	0.0
31	OH-	-1.0	1.08506E-08	-7.9645	1.08435E-08	-7.9648	9.99340E-01	-0.0003
33	H2 AQ	0.0	2.96477E-30	-29.5280	2.96477E-30	-29.5280	1.00000E+00	0.0000

---- LOOK MIN IAP ----

PHASE	LOG IAP	LOG KT	LOG IAP/KT
O2 GAS	-34.9651	-2.9369	-32.0281
H2 GAS	-29.5280	-3.1280	-26.4000

University of Alberta

STEP NUMBER 1

1.000E+00 MOLES OF REACTION HAVE BEEN ADDED.

REACTION IS:

0.61	MOLES OF CA	VALENCE =	0.0
0.25	MOLES OF S	VALENCE =	6.000
0.00	MOLES OF S	VALENCE =	-2.000
0.01	MOLES OF O2	VALENCE =	4.000
0.01	MOLES OF C	VALENCE =	4.000
0.00	MOLES OF P	VALENCE =	0.0
0.01	MOLES OF FE	VALENCE =	3.000
0.02	MOLES OF aaaaaaaa	VALENCE =	0.0

TOTAL MOLALITIES OF ELEMENTS

ELEMENT	MOLALITY	LOG MOLALITY	CONC MG/L
CA	6.117004E-01	-0.2135	24517.0
FE	5.635999E-03	-2.2490	314.8
C	6.643999E-03	-2.1776	405.4
S	2.518010E-01	-0.5989	24188.0
P	2.436000E-04	-3.6133	23.1

---- LOOK MIN IAP ----

PHASE	LOG IAP	LOG KT	LOG IAP/KT
CALCITE	-5.2480	-8.4460	3.1981
SIDERITE	-32.8553	-10.4834	-22.3719
GYPSUM	-3.1210	-4.6016	1.4807
HYDROXAP	17.5085	-2.9690	20.4775
HEMATITE	11.2921	-3.6224	14.9145
GOETHITE	5.6420	0.6810	4.9609
FEOH3A	5.6338	4.8910	0.7428
PYRITE	-279.8491	-18.6213	-261.2278
FES PPT	-161.4380	-3.9150	-157.5230
VIVIANIT	-104.5931	-36.0000	-68.5931
PCO2	-14.2818	-1.4071	-12.8746
O2 GAS	-5.3252	-2.9369	-2.3882
H2 GAS	-44.3562	-3.1280	-41.2282
CAOH2	-2.5374	-4.8854	2.3481

TOTAL MOLALITIES OF ELEMENTS

ELEMENT	MOLALITY	LOG MOLALITY	CONC MG/L

University of Alberta

CA	6.117004E-01	-0.2135	24517.0
FE	5.635999E-03	-2.2490	314.8
C	6.643999E-03	-2.1776	405.4
S	2.518010E-01	-0.5989	24188.0
P	2.436000E-04	-3.6133	23.1

----DESCRIPTION OF SOLUTION----

PH =	13.6141
PE =	7.0000
ACTIVITY H2O =	0.9813
IONIC STRENGTH =	0.9064
TEMPERATURE =	20.0000
ELECTRICAL BALANCE =	1.6909E-02
THOR =	1.5543E+00
TOTAL ALKALINITY =	7.0828E-01
ITERATIONS =	25
TDS MG/L =	49448.2

DISTRIBUTION OF SPECIES

I	SPECIES	Z	MOLALITY	LOG MOLALITY	ACTIVITY	LOG ACTIVITY	GAMMA	LOG GAMMA
1	H+	1.0	3.12794E-14	-13.5047	2.43178E-14	-13.6141	7.77437E-01	-0.1093
2	E-	-1.0	1.00000E-07	-7.0000	1.00000E-07	-7.0000	1.00000E+00	0.0
3	H2O	0.0	9.81292E-01	-0.0082	9.81292E-01	-0.0082	1.00000E+00	0.0
4	CA+2	2.0	1.52911E-01	-0.8156	3.80649E-02	-1.4195	2.48935E-01	-0.6039
8	FE+2	2.0	2.57333E-29	-28.5895	9.40063E-30	-29.0268	3.65310E-01	-0.4373
15	CO3-2	-2.0	7.76157E 04	-3.1101	1.48426E-04	-3.8285	1.91232E-01	-0.7184
16	SO4-2	-2.0	1.27237E-01	-0.8954	2.06484E-02	-1.6851	1.62283E-01	-0.7897
19	PO4-3	-3.0	1.82200E-08	-7.7395	1.89033E-09	-8.7235	1.03750E-01	-0.9840
31	OH-	-1.0	3.55121E-01	-0.4496	2.76085E-01	-0.5590	7.77437E-01	-0.1093
32	O2 AQ	0.0	3.83871E-06	-5.4158	4.72962E-06	-5.3252	1.23208E+00	0.0906
34	HCO3-	-1.0	1.29921E-07	-6.8863	8.59153E-08	-7.0659	6.61287E-01	-0.1796
35	H2CO3	0.0	4.16295E-15	-14.3806	5.12911E-15	-14.2900	1.23208E+00	0.0906
40	HSO4-	-1.0	5.46227E-14	-13.2626	4.24657E-14	-13.3720	7.77437E-01	-0.1093
65	HPO4-2	-2.0	3.08979E-10	-9.5101	1.12873E-10	-9.9474	3.65310E-01	-0.4373
66	H2PO4-	-1.0	5.85086E-17	-16.2328	4.54867E-17	-16.3421	7.77437E-01	-0.1093
75	CAOH+	1.0	3.28114E-01	-0.4840	2.55088E-01	-0.5933	7.77437E-01	-0.1093
76	CACO3	0.0	5.86768E-03	-2.2315	7.22947E-03	-2.1409	1.23208E+00	0.0906
77	CAHCO3+	1.0	3.74073E-08	-7.4270	2.90818E-08	-7.5364	7.77437E-01	-0.1093
78	CASO4	0.0	1.24564E-01	-0.9046	1.53474E-01	-0.8140	1.23208E+00	0.0906
79	CAPO4-	-1.0	2.43580E-04	-3.6134	1.89368E-04	-3.7227	7.77437E-01	-0.1093
80	CAHPO4	0.0	1.73868E-09	-8.7598	2.14220E-09	-8.6691	1.23208E+00	0.0906
81	CAH2PO4+	1.0	5.16706E-17	-16.2868	4.01706E-17	-16.3961	7.77437E-01	-0.1093
105	FEOH+	1.0	1.05523E-25	-24.9767	8.20374E-26	-25.0860	7.77437E-01	-0.1093
106	FEOH2	0.0	1.46945E-23	-22.8328	1.81048E-23	-22.7422	1.23208E+00	0.0906
107	FEOH3-	-1.0	3.32139E-20	-19.4787	2.58218E-20	-19.5880	7.77437E-01	-0.1093
108	FESO4	0.0	2.55283E-29	-28.5930	3.14531E-29	-28.5023	1.23208E+00	0.0906
116	FEOH+2	2.0	3.47808E-24	-23.4587	1.27058E-24	-23.8960	3.65310E-01	-0.4373
117	FEOH2+	1.0	2.94597E-14	-13.5308	2.29031E-14	-13.6401	7.77437E-01	-0.1093

University of Alberta

118	FEOH3	0.0	8.81293E-09	-8.0549	1.08583E-08	-7.9642	1.23208E+00	0.0906
119	FEOH4-	-1.0	5.63599E-03	-2.2490	4.38163E-03	-2.3584	7.77437E-01	-0.1093

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```
IMPOSE MINERAL CONSTRAINTS ON REACTION SOLUTION; S-8-1
0050011000 0 0          0.0
MINERALS
HEMATITE    3      6.00       -4.01       -30.8          0              0.0
 115    2.00        3    3.00         1   -6.00
HYDROXAP    4     0.0         -3.42       -36.2          0              0.0
   3    1.00       65    3.00         4    5.00         1   -4.00
CALCITE     2      4.00       -8.47       -2.58          1              0.0
  15    1.00        4    1.00
  1.3543E+01 -4.0100E-02 -3.0000E+03  0.0          0.0
GYPSUM      3      6.00       -4.60     -0.280E-01       0              0.0
   4    1.00       16    1.00         3    2.00
CAOH2       2     0.0         -4.93       -3.88          0              0.0
   4    1.00       31    2.00
MICROCLN    5     0.0          0.875      -12.5          0              0.0
  10    1.00       13    3.00         7    1.00         3   -4.00      1   -4.00
             0     0.0          0.0         0.0          0              0.0
```


University of Alberta

STEP NUMBER 1

TOTAL MOLALITIES OF ELEMENTS

ELEMENT	MOLALITY	LOG MOLALITY	CONC MG/L
CA	6.117004E-01	-0.2135	24517.0
FE	5.635999E-03	-2.2490	314.8
C	6.643999E-03	-2.1776	405.4
S	2.518010E-01	-0.5989	24188.0
P	2.436000E-04	-3.6133	23.1

----PHASE BOUNDARIES----

PHASE	DELTA PHASE*	LOG IAP	LOG KT	LOG IAP/KT
HEMATITE	-2.818000E-03	-3.6224	-3.6224	-0.0000
HYDROXAP	-8.119995E-05	-2.9690	-2.9690	-0.0000
CALCITE	-6.638809E-03	-8.4460	-8.4460	-0.0000
GYPSUM	-2.415162E-01	-4.6016	-4.6016	-0.0000
CAOH2	-3.072795E-01	-4.8854	-4.8854	-0.0000
MICROCLN	3.554078E-03	1.0309	1.0309	-0.0000

* NEGATIVE DELTA PHASE INDICATES PRECIPITATION AND POSITIVE DELTA PHASE INDICATES DISSOLUTION.

---- LOOK MIN IAP ----

PHASE	LOG IAP	LOG KT	LOG IAP/KT
CALCITE	-8.4460	-8.4460	-0.0000
SIDERITE	-40.2014	-10.4834	-29.7180
GYPSUM	-4.6016	-4.6016	-0.0000
HYDROXAP	-2.9690	-2.9690	-0.0000
CHALCEDY	-5.7908	-3.5807	-2.2101
QUARTZ	-5.7908	-4.0838	-1.7071
GIBBSITE	8.3298	9.0550	-0.7252
KAOLINIT	-42.0227	-37.5354	-4.4872
HEMATITE	-3.6224	-3.6224	-0.0000
GOETHITE	-1.8116	0.6810	-2.4927
FEOH3A	-1.8125	4.8910	-6.7035
PYRITE	-271.2780	-18.6213	-252.6567
FES PPT	-159.4502	-3.9150	-155.5352
VIVIANIT	-129.8476	-36.0000	-93.8476
PCO2	-15.1318	-1.4071	-13.7246
O2 GAS	-9.1407	-2.9369	-6.2037
H2 GAS	-42.4411	-3.1280	-39.3131
CAOH2	-4.8854	-4.8854	-0.0000
SILGEL	-5.7908	-3.0725	-2.7183
MICROCLN	1.0309	1.0309	-0.0000

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TOTAL MOLALITIES OF ELEMENTS

ELEMENT	MOLALITY	LOG MOLALITY	CONC MG/L
CA	5.585995E-02	-1.2529	2238.9
K	3.554078E-03	-2.4493	139.0
FE	2.297082E-11	-10.6388	0.0
AL	3.554078E-03	-2.4493	95.9
SI	1.066224E-02	-1.9722	640.6
C	5.190075E-06	-5.2848	0.3
S	1.028485E-02	-1.9878	988.0
P	1.523392E-10	-9.8172	0.0

----DESCRIPTION OF SOLUTION----

PH =	12.6565
PE =	7.0000
ACTIVITY H2O =	0.9980
IONIC STRENGTH =	0.1370
TEMPERATURE =	20.0000
ELECTRICAL BALANCE =	1.6909E-02
THOR =	6.1730E-02
TOTAL ALKALINITY =	8.1350E-02
ITERATIONS =	29
TDS MG/L =	4102.6

DISTRIBUTION OF SPECIES

I	SPECIES	Z	MOLALITY	LOG MOLALITY	ACTIVITY	LOG ACTIVITY	GAMMA	LOG GAMMA
1	H+	1.0	2.88075E-13	-12.5405	2.20528E-13	-12.6565	7.65521E-01	-0.1160
2	E-	-1.0	1.00000E-07	-7.0000	1.00000E-07	-7.0000	1.00000E+00	0.0
3	H2O	0.0	9.97967E-01	-0.0009	9.97967E-01	-0.0009	1.00000E+00	0.0
4	CA+2	2.0	3.77695E-02	-1.4229	1.35805E-02	-1.8671	3.59562E-01	-0.4442
7	K+	1.0	3.51228E-03	-2.4544	2.60631E-03	-2.5840	7.42057E-01	-0.1296
8	FE+2	2.0	6.94551E-34	-33.1583	2.38525E-34	-33.6225	3.43423E-01	-0.4642
10	AL+3	3.0	2.55428E-29	-28.5927	2.30613E-30	-29.6371	9.02849E-02	-1.0444
13	H4SIO4	0.0	1.56215E-06	-5.8063	1.61221E-06	-5.7926	1.03204E+00	0.0137
15	CO3-2	-2.0	7.48498E-07	-6.1258	2.63664E-07	-6.5789	3.52258E-01	-0.4531
16	SO4-2	-2.0	5.48923E-03	-2.2605	1.85013E-03	-2.7328	3.37048E-01	-0.4723
19	PO4-3	-3.0	3.61280E-14	-13.4422	3.26181E-15	-14.4865	9.02849E-02	-1.0444
31	OH-	-1.0	4.04449E-02	-1.3931	3.09614E-02	-1.5092	7.65521E-01	-0.1160
32	O2 AQ	0.0	7.00819E-10	-9.1544	7.23277E-10	-9.1407	1.03204E+00	0.0137
34	HCO3-	-1.0	1.79654E-09	-8.7456	1.38405E-09	-8.8588	7.70398E-01	-0.1133
35	H2CO3	0.0	7.13915E-16	-15.1464	7.36792E-16	-15.1327	1.03204E+00	0.0137
40	HSO4-	-1.0	4.50753E-14	-13.3461	3.45061E-14	-13.4621	7.65521E-01	-0.1160
65	HPO4-2	-2.0	5.14307E-15	-14.2888	1.76625E-15	-14.7529	3.43423E-01	-0.4642
66	H2PO4-	-1.0	8.43195E-21	-20.0741	6.45484E-21	-20.1901	7.65521E-01	-0.1160

University of Alberta

75	CAOH+	1.0	1.33322E-02	-1.8751	1.02061E-02	-1.9911	7.65521E-01	-0.1160
76	CACO3	0.0	4.43956E-06	-5.3527	4.58182E-06	-5.3390	1.03204E+00	0.0137
77	CAHCO3+	1.0	2.18341E-10	-9.6609	1.67145E-10	-9.7769	7.65521E-01	-0.1160
78	CASO4	0.0	4.75382E-03	-2.3230	4.90615E-03	-2.3093	1.03204E+00	0.0137
79	CAPO4-	-1.0	1.52286E-10	-9.8173	1.16578E-10	-9.9334	7.65521E-01	-0.1160
80	CAHPO4	0.0	1.15881E-14	-13.9360	1.19595E-14	-13.9223	1.03204E+00	0.0137
81	CAH2PO4+	1.0	2.65670E-21	-20.5757	2.03376E-21	-20.6917	7.65521E-01	-0.1160
100	KSO4-	-1.0	4.17969E-05	-4.3789	3.19964E-05	-4.4949	7.65521E-01	-0.1160
101	KHPO4-	-1.0	1.17252E-17	-16.9309	8.97590E-18	-17.0469	7.65521E-01	-0.1160
106	FEOH2	0.0	5.59796E-30	-29.2520	5.77734E-30	-29.2383	1.03204E+00	0.0137
107	FEOH3-	-1.0	1.20709E-27	-26.9183	9.24056E-28	-27.0343	7.65521E-01	-0.1160
116	FEOH+2	2.0	1.05275E-29	-28.9777	3.61540E-30	-29.4418	3.43423E-01	-0.4642
117	FEOH2+	1.0	9.54708E-21	-20.0201	7.30850E-21	-20.1362	7.65521E-01	-0.1160
118	FEOH3	0.0	3.76509E-16	-15.4242	3.88574E-16	-15.4105	1.03204E+00	0.0137
119	FEOH4-	-1.0	2.29704E-11	-10.6388	1.75844E-11	-10.7549	7.65521E-01	-0.1160
150	ALOH+2	2.0	2.20770E-22	-21.6561	7.58175E-23	-22.1202	3.43423E-01	-0.4642
151	ALOH2+	1.0	4.90041E-15	-14.3098	3.75137E-15	-14.4258	7.65521E-01	-0.1160
152	ALOH3	0.0	2.07083E-08	-7.6839	2.13719E-08	-7.6702	1.03204E+00	0.0137
153	ALOH4-	-1.0	3.55406E-03	-2.4493	2.72071E-03	-2.5653	7.65521E-01	-0.1160
154	ALSO4+	1.0	5.48596E-30	-29.2607	4.19962E-30	-29.3768	7.65521E-01	-0.1160
170	H3SIO4-	-1.0	8.67199E-04	-3.0619	6.63859E-04	-3.1779	7.65521E-01	-0.1160
171	H2SIO4-2	-2.0	9.79347E-03	-2.0091	3.36330E-03	-2.4732	3.43423E-01	-0.4642

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```
AFBC SAMPLE S-B-1.  OPEN SYSTEM, FIX CO2 AT ATMOSPHERIC.
0040011000 1 8          0.0
SOLUTION 1
DIST. WATER WITH 8 COMPONENT REACTION, NO MINERAL CONSTRAINTS. S-B-1
 0  0 2      6.20       7.00       20.0       1.00
STEPS
  1.00
REACTION
    4   0.612    0.0    16   0.247   6.000   16   0.005  -2.000   32   0.010   4.000
   15   0.007   4.000   19   0.000   0.0      8   0.006   3.000    0   0.017   0.0
```

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SOLUTION NUMBER 1 DIST. WATER WITH 8 COMPONENT REACTION, NO MINERAL CONSTRAINTS. S-B-1

TOTAL MOLALITIES OF ELEMENTS

ELEMENT	MOLALITY	LOG MOLALITY	CONC MG/L

PURE WATER

----DESCRIPTION OF SOLUTION----

PH =	6.2000
PE =	7.0000
ACTIVITY H2O =	1.0000
IONIC STRENGTH =	0.0000
TEMPERATURE =	20.0000
ELECTRICAL BALANCE =	6.2052E-07
THOR =	-5.9295E-30
TOTAL ALKALINITY =	1.0851E-08
ITERATIONS =	5
TDS MG/L =	0.0

DISTRIBUTION OF SPECIES

I	SPECIES	Z	MOLALITY	LOG MOLALITY	ACTIVITY	LOG ACTIVITY	GAMMA	LOG GAMMA
1	H+	1.0	6.31374E-07	-6.1997	6.30957E-07	-6.2000	9.99340E-01	-0.0003
2	E-	-1.0	1.00000E-07	-7.0000	1.00000E-07	-7.0000	1.00000E+00	0.0
3	H2O	0.0	1.00000E+00	-0.0000	1.00000E+00	-0.0000	1.00000E+00	0.0
31	OH-	-1.0	1.08506E-08	-7.9645	1.08435E-08	-7.9648	9.99340E-01	-0.0003
33	H2 AQ	0.0	2.96477E-30	-29.5280	2.96477E-30	-29.5280	1.00000E+00	0.0000

---- LOOK MIN IAP ----

PHASE	LOG IAP	LOG KT	LOG IAP/KT
O2 GAS	-34.9651	-2.9369	-32.0281
H2 GAS	-29.5280	-3.1280	-26.4000

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STEP NUMBER 1

1.000E+00 MOLES OF REACTION HAVE BEEN ADDED.

REACTION IS:

0.61 MOLES OF CA	VALENCE =	0.0
0.25 MOLES OF S	VALENCE =	6.000
0.00 MOLES OF S	VALENCE =	-2.000
0.01 MOLES OF O2	VALENCE =	4.000
0.01 MOLES OF C	VALENCE =	4.000
0.00 MOLES OF P	VALENCE =	0.0
0.01 MOLES OF FE	VALENCE =	3.000
0.02 MOLES OF aaaaaaaa	VALENCE =	0.0

TOTAL MOLALITIES OF ELEMENTS

ELEMENT	MOLALITY	LOG MOLALITY	CONC MG/L
CA	6.117004E-01	-0.2135	24517.0
FE	5.635999E-03	-2.2490	314.8
C	6.643999E-03	-2.1776	405.4
S	2.518010E-01	-0.5989	24188.0
P	2.436000E-04	-3.6133	23.1

---- LOOK MIN IAP ----

PHASE	LOG IAP	LOG KT	LOG IAP/KT
CALCITE	-5.2480	-8.4460	3.1981
SIDERITE	-32.8553	-10.4834	-22.3719
GYPSUM	-3.1210	-4.6016	1.4807
HYDROXAP	17.5085	-2.9690	20.4775
HEMATITE	11.2921	-3.6224	14.9145
GOETHITE	5.6420	0.6810	4.9609
FEOH3A	5.6338	4.8910	0.7428
PYRITE	-279.8491	-18.6213	-261.2278
FES PPT	-161.4380	-3.9150	-157.5230
VIVIANIT	-104.5931	-36.0000	-68.5931
PCO2	-14.2818	-1.4071	-12.8746
O2 GAS	-5.3252	-2.9369	-2.3882
H2 GAS	-44.3562	-3.1280	-41.2282
CAOH2	-2.5374	-4.8854	2.3481

TOTAL MOLALITIES OF ELEMENTS

ELEMENT	MOLALITY	LOG MOLALITY	CONC MG/L

University of Alberta

CA	6.117004E-01	-0.2135	24517.0
FE	5.635999E-03	-2.2490	314.8
C	6.643999E-03	-2.1776	405.4
S	2.518010E-01	-0.5989	24188.0
P	2.436000E-04	-3.6133	23.1

----DESCRIPTION OF SOLUTION----

PH =	13.6141
PE =	7.0000
ACTIVITY H2O =	0.9813
IONIC STRENGTH =	0.9064
TEMPERATURE =	20.0000
ELECTRICAL BALANCE =	1.6909E-02
THOR =	1.5543E+00
TOTAL ALKALINITY =	7.0828E-01
ITERATIONS =	25
TDS MG/L =	49448.2

DISTRIBUTION OF SPECIES

I	SPECIES	Z	MOLALITY	LOG MOLALITY	ACTIVITY	LOG ACTIVITY	GAMMA	LOG GAMMA
1	H+	1.0	3.12794E-14	-13.5047	2.43178E-14	-13.6141	7.77437E-01	-0.1093
2	E-	-1.0	1.00000E-07	-7.0000	1.00000E-07	-7.0000	1.00000E+00	0.0
3	H2O	0.0	9.81292E-01	-0.0082	9.81292E-01	-0.0082	1.00000E+00	0.0
4	CA+2	2.0	1.52911E-01	-0.8156	3.80649E-02	-1.4195	2.48935E-01	-0.6039
8	FE+2	2.0	2.57333E-29	-28.5895	9.40063E-30	-29.0268	3.65310E-01	-0.4373
15	CO3-2	-2.0	7.76157E-04	-3.1101	1.48426E-04	-3.8285	1.91232E-01	-0.7184
16	SO4-2	-2.0	1.27237E-01	-0.8954	2.06484E-02	-1.6851	1.62283E-01	-0.7897
19	PO4-3	-3.0	1.82200E-08	-7.7395	1.89033E-09	-8.7235	1.03750E-01	-0.9840
31	OH-	-1.0	3.55121E-01	-0.4496	2.76085E-01	-0.5590	7.77437E-01	-0.1093
32	O2 AQ	0.0	3.83871E-06	-5.4158	4.72962E-06	-5.3252	1.23208E+00	0.0906
34	HCO3-	-1.0	1.29921E-07	-6.8863	8.59153E-08	-7.0659	6.61287E-01	-0.1796
35	H2CO3	0.0	4.16295E-15	-14.3806	5.12911E-15	-14.2900	1.23208E+00	0.0906
40	HSO4-	-1.0	5.46227E-14	-13.2626	4.24657E-14	-13.3720	7.77437E-01	-0.1093
65	HPO4-2	-2.0	3.08979E-10	-9.5101	1.12873E-10	-9.9474	3.65310E-01	-0.4373
66	H2PO4-	-1.0	5.85086E-17	-16.2328	4.54867E-17	-16.3421	7.77437E-01	-0.1093
75	CAOH+	1.0	3.28114E-01	-0.4840	2.55088E-01	-0.5933	7.77437E-01	-0.1093
76	CACO3	0.0	5.86768E-03	-2.2315	7.22947E-03	-2.1409	1.23208E+00	0.0906
77	CAHCO3+	1.0	3.74073E-08	-7.4270	2.90818E-08	-7.5364	7.77437E-01	-0.1093
78	CASO4	0.0	1.24564E-01	-0.9046	1.53474E-01	-0.8140	1.23208E+00	0.0906
79	CAPO4-	-1.0	2.43580E-04	-3.6134	1.89368E-04	-3.7227	7.77437E-01	-0.1093
80	CAHPO4	0.0	1.73868E-09	-8.7598	2.14220E-09	-8.6691	1.23208E+00	0.0906
81	CAH2PO4+	1.0	5.16706E-17	-16.2868	4.01706E-17	-16.3961	7.77437E-01	-0.1093
105	FEOH+	1.0	1.05523E-25	-24.9767	8.20374E-26	-25.0860	7.77437E-01	-0.1093
106	FEOH2	0.0	1.46945E-23	-22.8328	1.81048E-23	-22.7422	1.23208E+00	0.0906
107	FEOH3-	-1.0	3.32139E-20	-19.4787	2.58218E-20	-19.5880	7.77437E-01	-0.1093
108	FESO4	0.0	2.55283E-29	-28.5930	3.14531E-29	-28.5023	1.23208E+00	0.0906
116	FEOH+2	2.0	3.47808E-24	-23.4587	1.27058E-24	-23.8960	3.65310E-01	-0.4373
117	FEOH2+	1.0	2.94597E-14	-13.5308	2.29031E-14	-13.6401	7.77437E-01	-0.1093

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118	FEOH3	0.0	8.81293E-09	-8.0549	1.08583E-08	-7.9642	1.23208E+00	0.0906
119	FEOH4-	-1.0	5.63599E-03	-2.2490	4.38163E-03	-2.3584	7.77437E-01	-0.1093

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```
IMPOSE MINERAL CONSTRAINTS ON REACTION SOLUTION, S-B-1
0050010000 0 0          0.0
MINERALS
FIX PCO2     2      4.00      -1.47      -4.71          0              -3.500
  35    1.00         3   -1.00
CALCITE      2      4.00      -8.47      -2.58          1               0.0
  15    1.00         4    1.00
  1.3543E+01 -4.0100E-02 -3.0000E+03  0.0             0.0
HEMATITE     3      6.00      -4.01      -30.8          0               0.0
 115    2.00         3    3.00          1   -6.00
HYDROXAP     4      0.0       -3.42      -36.2          0               0.0
   3    1.00        65    3.00          4    5.00      1   -4.00
GYPSUM       2      6.00      -4.60     -0.280E-01      0               0.0
  16    1.00         4    1.00
               0    0.0        0.0        0.0           0               0.0
```

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STEP NUMBER 1

TOTAL MOLALITIES OF ELEMENTS

ELEMENT	MOLALITY	LOG MOLALITY	CONC MG/L
CA	6.117004E-01	-0.2135	24517.0
FE	5.635999E-03	-2.2490	314.8
C	6.643999E-03	-2.1776	405.4
S	2.518010E-01	-0.5989	24188.0
P	2.436000E-04	-3.6133	23.1

----PHASE BOUNDARIES----

PHASE	DELTA PHASE*	LOG IAP	LOG KT	LOG IAP/KT
FIX PCO2	3.445601E-01	-4.9111	-1.4111	-3.5000
CALCITE	-3.508805E-01	-8.4460	-8.4460	-0.0000
HEMATITE	-2.818000E-03	-3.6224	-3.6224	-0.0000
HYDROXAP	-8.115300E-05	-2.9690	-2.9690	-0.0000
GYPSUM	-2.400442E-01	-4.6016	-4.6016	-0.0000

* NEGATIVE DELTA PHASE INDICATES PRECIPITATION AND POSITIVE DELTA PHASE INDICATES DISSOLUTION.

---- LOOK MIN IAP ----

PHASE	LOG IAP	LOG KT	LOG IAP/KT
CALCITE	-8.4460	-8.4460	-0.0000
SIDERITE	-24.9964	-10.4834	-14.5130
GYPSUM	-4.6021	-4.6016	-0.0004
HYDROXAP	-2.9690	-2.9690	-0.0000
HEMATITE	-3.6224	-3.6224	-0.0000
GOETHITE	-1.8113	0.6810	-2.4923
FEOH3A	-1.8115	4.8910	-6.7025
PYRITE	-176.0831	-18.6213	-157.4618
FES PPT	-104.3772	-3.9150	-100.4622
VIVIANIT	-80.8201	-36.0000	-44.8201
PCO2	-4.9111	-1.4071	-3.5040
O2 GAS	-29.0756	-2.9369	-26.1386
H2 GAS	-32.4730	-3.1280	-29.3450
CAOH2	-15.1061	-4.8854	-10.2207

TOTAL MOLALITIES OF ELEMENTS

ELEMENT	MOLALITY	LOG MOLALITY	CONC MG/L

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CA	2.036999E-02	-1.6910	816.4
FE	1.458484E-15	-14.8361	0.0
C	3.236828E-04	-3.4899	19.8
S	1.175680E-02	-1.9297	1129.4
P	1.410012E-07	-6.8508	0.0

----DESCRIPTION OF SOLUTION----

PH =	7.6725
PE =	7.0000
ACTIVITY H2O =	0.9995
IONIC STRENGTH =	0.0450
TEMPERATURE =	20.0000
ELECTRICAL BALANCE =	1.6909E-02
THOR =	7.1836E-02
TOTAL ALKALINITY =	3.1765E-04
ITERATIONS =	39
TDS MG/L =	1965.5

DISTRIBUTION OF SPECIES

I	SPECIES	Z	MOLALITY	LOG MOLALITY	ACTIVITY	LOG ACTIVITY	GAMMA	LOG GAMMA
1	H+	1.0	2.56660E-08	-7.5906	2.12578E-08	-7.6725	8.28248E-01	-0.0818
2	E-	-1.0	1.00000E-07	-7.0000	1.00000E-07	-7.0000	1.00000E+00	0.0
3	H2O	0.0	9.99531E-01	-0.0002	9.99531E-01	-0.0002	1.00000E+00	0.0
4	CA+2	2.0	1.55100E-02	-1.8094	7.56855E-03	-2.1210	4.87979E-01	-0.3116
8	FE+2	2.0	4.52940E-19	-18.3440	2.13148E-19	-18.6713	4.70588E-01	-0.3274
15	CO3-2	-2.0	9.71688E-07	-6.0125	4.73100E-07	-6.3250	4.86885E-01	-0.3126
16	SO4-2	-2.0	6.92095E-03	-2.1598	3.30627E-03	-2.4807	4.77719E-01	-0.3208
19	PO4-3	-3.0	2.15929E-12	-11.6657	3.96053E-13	-12.4022	1.83418E-01	-0.7366
31	OH-	-1.0	3.88405E-07	-6.4107	3.21695E-07	-6.4926	8.28248E-01	-0.0818
32	O2 AQ	0.0	8.31646E-30	-29.0801	8.40311E-30	-29.0756	1.01042E+00	0.0045
34	HCO3-	-1.0	2.86585E-04	-3.5427	2.39392E-04	-3.6209	8.35327E-01	-0.0781
35	H2CO3	0.0	1.21388E-05	-4.9158	1.22653E-05	-4.9113	1.01042E+00	0.0045
40	HSO4-	-1.0	7.17672E-09	-8.1441	5.94410E-09	-8.2259	8.28248E-01	-0.0818
65	HPO4-2	-2.0	4.39300E-08	-7.3572	2.06730E-08	-7.6846	4.70588E-01	-0.3274
66	H2PO4-	-1.0	8.79290E-09	-8.0559	7.28270E-09	-8.1377	8.28248E-01	-0.0818
75	CAOH+	1.0	7.13544E-08	-7.1466	5.90992E-08	-7.2284	8.28248E-01	-0.0818
76	CACO3	0.0	4.53458E-06	-5.3435	4.58182E-06	-5.3390	1.01042E+00	0.0045
77	CAHCO3+	1.0	1.94531E-05	-4.7110	1.61120E-05	-4.7929	8.28248E-01	-0.0818
78	CASO4	0.0	4.83584E-03	-2.3155	4.88623E-03	-2.3110	1.01042E+00	0.0045
79	CAPO4-	-1.0	9.52470E-09	-8.0211	7.88881E-09	-8.1030	8.28248E-01	-0.0818
80	CAHPO4	0.0	7.72074E-08	-7.1123	7.80119E-08	-7.1078	1.01042E+00	0.0045
81	CAH2PO4+	1.0	1.54399E-09	-8.8114	1.27881E-09	-8.8932	8.28248E-01	-0.0818
105	FEOH+	1.0	2.61685E-21	-20.5822	2.16740E-21	-20.6641	8.28248E-01	-0.0818
106	FEOH2	0.0	5.51597E-25	-24.2584	5.57344E-25	-24.2539	1.01042E+00	0.0045
107	FEOH3-	-1.0	1.11830E-27	-26.9514	9.26228E-28	-27.0333	8.28248E-01	-0.0818
108	FESO4	0.0	1.13015E-19	-18.9469	1.14193E-19	-18.9424	1.01042E+00	0.0045
111	FEHPO4	0.0	1.73613E-23	-22.7604	1.75422E-23	-22.7559	1.01042E+00	0.0045
112	FEH2PO4+	1.0	9.39346E-25	-24.0272	7.78011E-25	-24.1090	8.28248E-01	-0.0818

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115	FE+3	3.0	8.09514E-25	-24.0918	1.48480E-25	-24.8283	1.83418E-01	-0.7366
116	FEOH+2	2.0	7.13324E-20	-19.1467	3.35682E-20	-19.4741	4.70588E-01	-0.3274
117	FEOH2+	1.0	8.51263E-16	-15.0699	7.05057E-16	-15.1518	8.28248E-01	-0.0818
118	FEOH3	0.0	3.85471E-16	-15.4140	3.89487E-16	-15.4095	1.01042E+00	0.0045
119	FEOH4-	-1.0	2.21111E-16	-15.6554	1.83135E-16	-15.7372	8.28248E-01	-0.0818
125	FESO4+	1.0	4.42552E-24	-23.3540	3.66542E-24	-23.4359	8.28248E-01	-0.0818
126	FESO42-	-1.0	4.53603E-25	-24.3433	3.75696E-25	-24.4252	8.28248E-01	-0.0818
127	FEHPO4+	1.0	8.37338E-28	-27.0771	6.93523E-28	-27.1589	8.28248E-01	-0.0818
128	FEH2P+2	2.0	6.17055E-28	-27.2097	2.90379E-28	-27.5370	4.70588E-01	-0.3274

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APPENDIX C

Section 1 - Duplicate Analyses of Aquatic Toxicity and Genotoxicity Tests

Section 2 - Multi-detector Laser Light Scattering Analysis

1. Duplicate Analyses of Aquatic Toxicity and Genotoxicity Tests [1,2]

1. Microtox™:

SAMPLE	5 min. EC_{50} (% v/v)	15 min. EC_{50} (% v/v)
(a) Untreated Samples:		
bed run #5 replicate #1	0.63 (0.56-0.71)	0.66 (0.60-0.73)
bed run #5 replicate #2	0.82 (0.69-0.97)	0.83 (0.68-1.02)
cyclone #1 replicate #1	0.51 (0.45-0.58)	0.65 (0.53-0.80)
cyclone #1 replicate #2	0.80 (0.70-0.90)	0.85 (0.73-0.98)
cyclone #2 replicate #1	0.77 (0.70-0.84)	0.78 (0.67-0.92)
cyclone #2 replicate #2	0.43 (0.30-0.62)	0.49 (0.35-0.68)
cyclone #5 replicate #1	0.71 (0.62-0.82)	0.75 (0.66-0.84)
cyclone #5 replicate #2	0.54 (0.51-0.57)	0.56 (0.53-0.60)
cyclone #8 replicate #1	0.94 (0.80-1.10)	0.88 (0.74-1.05)
cyclone #8 replicate #2	0.78 (0.67-0.91)	0.84 (0.72-0.98)
(b) Treated Samples:		
bed run #8 replicate #1	Not toxic	Not toxic
bed run #8 replicate #2	Not toxic	Not toxic
baghouse #1 replicate #1	Not toxic	Not toxic
baghouse #1 replicate #2	Not toxic	Not toxic

2. Selenastrum capricornutum:

(a) Untreated Samples:	4 day EC_{50} (% v/v)
bed run #8 replicate #1	20 [11-46]
bed run #8 replicate #2	10
cyclone #8 replicate #1	30 [23-91]
cyclone #8 replicate #2	10 [5.6-2.3]
(b) Treated Samples:	
bed run #8 replicate #1	Not toxic
bed run #8 replicate #2	Not toxic
cyclone #8 replicate #1	Not toxic
cyclone #8 replicate #2	Not toxic

3. SOS Chromotest™:

(a) Untreated Samples:	Genotoxic Threshold (% v/v)
cyclone #5 replicate #1	Not genotoxic
cyclone #5 replicate #2	Not genotoxic
baghouse #5 replicate #1	Not genotoxic
baghouse #5 replicate #2	Not genotoxic
(b) Treated Samples:	
cyclone #5 replicate #1	Not genotoxic
cyclone #5 replicate #2	Not genotoxic
baghouse #5 replicate #1	Not genotoxic
baghouse #5 replicate #2	Not genotoxic

4. Daphnia magna:	
(a) Untreated Samples:	48 hour LC_{50} (% v/v)
bed run #5 replicate #1	1.8 (1.28-2.31)
bed run #5 replicate #2	1.4 (1.01-1.85)
bed run #8 replicate #1	7.8 (6.13-10.0)
bed run #8 replicate #2	7.4 (5.79-9.41)
(b) Treated Samples:	Insufficient sample remained for duplicate testing.

1. Microtox EC_{50}'s indicate the % sample volume which caused a 50% reduction in light (linked to cell respiration) produced by the luminescent bacterium *Photobacterium phosphoreum*. The sample concentration above which toxicity could not be detected was 45.5%.

   Selenastrum capricornutum EC_{50}'s indicate the % sample which caused a 50% inhibition in the growth of this algal species during a 96-hour period. The sample concentration above which toxicity could not be detected was 91% .

   Daphnia magna LC_{50}'s indicate the % sample volume caused a 50% mortality rate after an exposure period of 48 hours.

   The SOS Chromotest™ procedure provides the threshold sample concentration which causes induction of the SOS DNA repair genes in a genetically engineered strain of *E. coli*. The endpoint in the procedure above which genotoxicity cannot be detected was 9.1% sample volume.

2. In brackets below each toxicity result are 95% confidence limits. In the case of the algal assays and some of the *Daphnia* tests, inadequate data were available to provide 95% confidence limits. When this occurred, the numbers in brackets are the intervals of sample concentration between which no effect and total (100%) effect were observed. These intervals are indicated by square brackets.

2. Multi-Detector Laser Light Scattering Analyses

Technical Background

As a supplement to the battery of toxicity tests, the algal assays were also analyzed by multi-detector light scattering using a Wyatt photometer (Wyatt Technology Corporation, Santa Barbara, California). Conventional light scattering instruments measure light scattered by particles in fluids by means of a single detector placed at right angles to the light source. However, the Wyatt Instrument has 18 detectors set at different angles around the sample cell. With the aid of a computer interface, 1 700 complete angular scans per second can be measured. Plots of detector outputs produce characteristic "fingerprints" of complex particle suspensions and can provide information on changes in cell shape and integrity (1).

Results

(a) Detection of Abnormal Morphological Changes during the 4-day Algal Growth Inhibition Assay

In algal assays conducted on leachates from volcanic ashes, atypically-shaped cells were produced (2). This was a sub-lethal effect in that the leachates did not interfere with the growth of the algae.

The samples from the algal assay were analyzed for morphological changes both by laser light scattering analysis and by microscopic examination. The analyses were conducted at no-effect and slight toxic effect concentrations for growth inhibition.

No change in cell morphology was detected as a consequence of leachate exposure by either method.

(b) Rapid Detection of Acute Toxicity in Algal Assays

A trial experiment was also conducted to determine if the multi-detector laser light photometer could be useful for acute toxicity.

A microplate algal assay was prepared for leachate from bed sample Run No. 2. The pH of this leachate was pH 12.2. To ensure that the toxicity due to the high pH of the sample was not neutralized, algae were added in an algal broth medium instead of bicarbonate. After four hours of incubation, the algal exposed to dilutions of the leachate were analyzed by the Wyatt photometer.

The results are shown in Figure 1. The results were normalized to the detector No. 5 output in order to demonstrate changes in the light scattering "fingerprint" of the algae exposed to the leachate. It can be seen that alterations in the "fingerprint" did occur as a consequence of exposure to the leachate and were maximal at detector No. 3. In most cases, the degree of "fingerprint" change was related to the strength of the leachate concentration.

This technique, therefore, may have potential as a rapid acute toxicity testing method.

References

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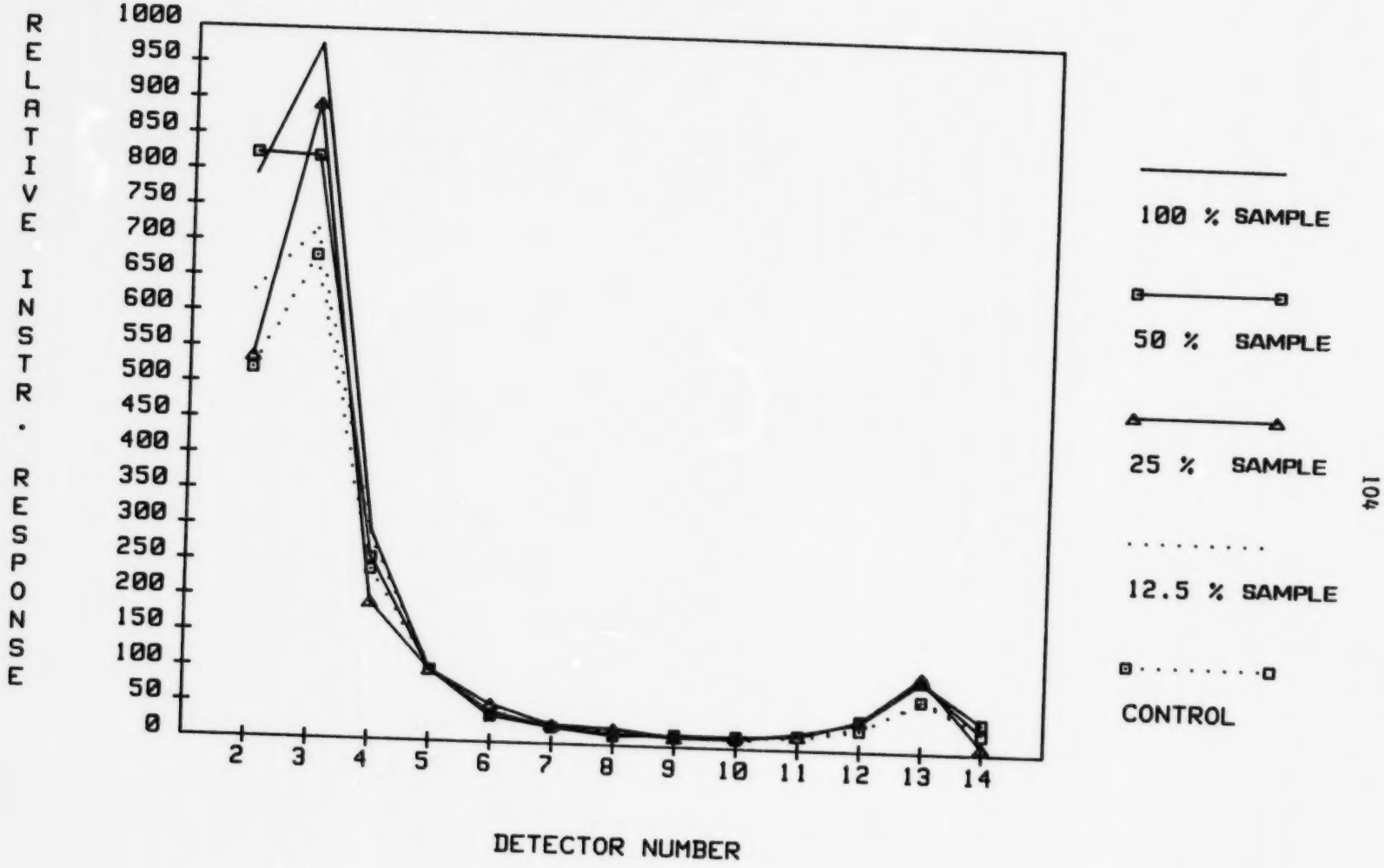

FIGURE 1 FOUR-HOUR ALGAL TOXICITY ASSAY BY LASER PHOTOMETER